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## THE COLLOID ASPECTS OF TEXTILE MATERIALS AND RELATED TOPICS.

#### A GENERAL DISCUSSION.

The Second Colloid Meeting organised by the Colloid Committee of the Faraday Society, being the Fifty-Seventh General Discussion organised by the Faraday Society, was devoted to the discussion of "The Colloid Aspects of Textile Materials and related Topics."

The Colloid Committee comprises, in addition to representatives of the Faraday Society, representatives also from the Royal Society, the Biochemical Society, the Chemical Society, the Physical Society,

the Physiological Society and the Society of Chemical Industry.

The meeting, which was attended by about 260 members of the various societies and visitors, was held by kind permission of the University authorities and Professor A. Lapworth, F.R.S., in the Chemistry Theatre of the University of Manchester from Wednesday to Friday, the 21st to 23rd September, 1932. The President of the Faraday Society, Sir Robert Mond, occupied the Chair throughout the meeting.

On Tuesday evening the 20th September, the President entertained the overseas members and visitors to dinner at the Dorchester Hotel, London. The party of thirty included the following distinguished overseas workers in the field under discussion, and in four cases their wives:—

Professor E. H. Buchner, Amsterdam, Professor E. Elöd and Frau Elöd, Karlsruhe, Professor R. O. Herzog, Berlin, Dr. J. R. Katz and Mrs. Katz, Amsterdam, Professor P. Krais, Dresden, Professor H. Lecher and Frau Lecher, Dresden, Professor H. Mark, Wien, Professor O. Roehrich, Paris, Dr. H. de Witt Smith, New York, Professor H. Staudinger and Frau Staudinger, Freiburg i. B.

During the evening letters of greeting were sent to Lady Mond, who had been unable to return from France, and to Professor Ostwald, whose activities in connection with the organisation of an impending meeting of the Kolloid-Gesellschaft precluded him from making the

journey to England.

The social headquarters of the Society in Manchester were at the Midland Hotel, where a large party met for an informal dinner on the evening of Thursday, the 22nd September. The guests of the Society, in addition to the overseas guests named above and below, included Dr. Mouat Jones, Principal of the College of Technology (who replied to the toast of the City of Manchester proposed by the President), Mr. D. C. Henry (representing the University) and Mrs. Henry, and Messrs. Kershaw and Barwick (representing the Textile Institute). The toast of the President was proposed by Professor Krais.

During the meeting, luncheon and tea were taken daily at the University refectory. After the business session on Thursday afternoon the members visited the House of the Manchester Literary and Philosophical Society, where they were shown the treasures of the Society under the guidance of the President (Dr. Mouat Jones), the Secretary (Mr. Henry), and members of the Council. During Friday afternoon members visited the laboratories and part of the factories of Messrs. Tootal, Broadhurst, Lee, Co., Ltd., and also the Research Laboratories of the Metropolitan Vickers Electrical Co., Ltd., tea being provided for each party by the kindness of the directors. The ladies guests of the Society, with Mlle Jeanne le Manach, the President's niece, in addition to taking part in these social functions (as well as in some part of the business meetings) were given an opportunity of seeing some of the beauty of Derbyshire during a motor tour under the guidance of Mrs. Henry.

At the inaugural session at 2.30 p.m. on Wednesday, 21st September, the Society was welcomed on behalf of the University by Mr. Henry, and then the President extended a welcome to the President of the Textile Institute (Mr. G. Garnett), who replied.

The President expressed the Society's regret at the absence of Professor Ostwald, Dr. Sheppard and Dr. Trillat, and then introduced the overseas members and guests individually to the Society, calling upon them, in accordance with a time-honoured custom of the Society, to rise in their seats, whereupon they were welcomed with acclamation & by the Society. Those so greeted included those above-mentioned as well as the following, who had been unable to accept the President's hospitality in London: Dr. G. van Iterson (Delft), Fräulein Dr. Krüger (Berlin), Dr. Hans Machemer (Berlin), and Dr. M. Mathieu (Paris).

Professor F. G. Donnan then delivered an Introductory Address, after which Professor H. Mark delivered a General Introduction to the

subject under discussion.

The contributions, which had all been circulated in advance, were taken as read, the authors each devoting a few minutes to indicating the lines upon which they deemed their contributions called for discussion, whereupon the papers were discussed, for the most part individually, under the following heads and sub-heads:—

Part I. General: Raw Materials and their Constitution.
(a) Cellulose, (b) Cellulose Derivatives, (c) Lignin, Keratin, etc.
Part II. Fibre Particles, their Production, Deformation and

Degradation.

Part III. Manufacturing Processes.

The contributions and a report of the discussion thereon will be found in the succeeding pages.

At the close of the business session on Friday, 23rd September, the President expressed the hearty thanks of all present to the many distinguished members and visitors who had travelled from overseas to give their papers and to contribute, both during the meeting and informally during times not set aside for business, their views on the topics under discussion. The thanks of the members were accorded with acclamation. Votes of thanks were also cordially carried to the University of Manchester and Professor Lapworth, to the organising committee and especially to Mr. Henry, to the staff of the chemical department and of the refectory, and to the Manchester Literary and Philosophical Society and the directors of Messrs. Tootal, Broadhurst,

Lee, Co., Ltd., and of Messrs. The Metropolitan Vickers Electrical Co., Ltd.

Before the meeting finally closed Professor Krais expressed to the President the thanks of his overseas guests for his abundant and kindly hospitality, and Professor Donnan expressed the particular thanks of the Faraday Society for all his work, first for many years as Honorary Treasurer and then for two years as President. The Society's General Discussions had reached a high stage of interest and importance under his guidance as President, which had an immense effect on the international prestige of the Society. The President, in reply, thanked the Society for having given him the opportunity to serve it. Though the present meeting was the last over which he might preside in the office of President, he would always continue to seek the advantage of the Society. His years of office had been happy, and, he believed, fruitful, and he wished the Society all the success in the future it so well merited.

### INTRODUCTORY ADDRESS.

PROFESSOR F. G. DONNAN, F.R.S.

Several years ago the Faraday Society, at the instigation of Sir William Hardy, formed a special Colloid Committee, for the purpose of organising Discussions in this branch of physico-chemical science. In order to ensure as wide a scope as possible, the Faraday Society has invited other Societies to join in this work, with the very satisfactory result that the Royal Society, the Chemical Society, the Society of Chemical Industry, the Physical Society, the Biochemical Society and the Physiological Society are represented on the Colloid Committee. For the present, our discussion is arranged to take place every two The first one, dealing with Colloid Science in relation to Biology and Physiology, was held at Cambridge two years ago and was very successful. It was felt that the second one should have a close relation to some subject of great technical importance, and so the Committee arranged the present discussion. Meeting here at Manchester, it is unnecessary to emphasise the importance of textile fibres and materials. Great advances have been made during recent years in the scientific study of the inner structure and properties of these naturally-occurring substances.

We are exceedingly fortunate in having with us on this occasion many of the most eminent investigators in this field of research. The Organising Sub-Committee may indeed be congratulated on having assembled a veritable galaxy of stars of the first magnitude. If Professors Freundlich, Kurt Hess, Kurt Meyer, Ostwald and Trillat could have been present, we should have been able to say that very nearly all the stars had come to Manchester for this discussion. As it is, we have with us a most distinguished gathering of eminent foreign men of science and can look forward to a highly interesting and valuable meeting. Indeed with Professor Mark and Professor Staudinger both present we may be the witnesses of a conflict of giants! We can congratulate ourselves very heartily on the presence of Professor R. O. Herzog. To his leadership and influence is due the whole modern

development of the study of fibres and textile materials. We are fortunate, too, in having with us Dr. Katz, from Amsterdam, whom I might call the "König der Quellung." His important survey of the subject of swelling forms a most valuable contribution to the discussion. We are also very glad to see amongst us Professor Elöd, whose work on the action of dyes and mordants in relation to textile materials forms a very valuable advance in our understanding of these highly important phenomena.

To all the foreign men of science who have come over to England for this meeting, as well as to the numerous British workers who are with us to-day, the Faraday Society and the Colloid Committee offer

a hearty welcome.

### GENERAL INTRODUCTION.

### By Professor Hermann Mark.

I wish first to express my sincerest appreciation of the great honour which has been conferred upon me by the invitation to give a general introduction to the first part of the present meeting. I feel that I cannot fulfil my task better than by giving a very brief survey of the material which will be discussed this afternoon.

I will not say anything about the first paper, because I shall have myself the honour to present it, and to answer questions related to its content.

After this we shall discuss a paper of Prof. Haworth and Dr. Hirst, applying in a most ingenious way the well-known and well-founded classical methods of preparative organic chemistry in order to work out the length of the main valence chains of cellulose. It is of the utmost interest to see how they have succeeded in separating traces of tetramethylglucose from a large amount of trimethylglucose; it is striking that they have arrived at the same order of magnitude for the length of the chains, as has been deduced by the X-ray method. Our ideas are led in the same direction by the results, which Dr. Büchner has obtained by very careful observations of the osmotic pressure of nitrated and acetylated cellulose.

This fact increases the interest in the paper of Prof. Staudinger, who attained another result by means of his careful viscosity measurements. He indeed has been able to deduce several very suggestive laws for the viscosity of diluted solutions of fibre molecules, and has applied these laws in a very interesting and convincing way to the structure of the cellulose. There is no doubt that this discrepancy in the question of the chain-length will lead to a number of new investigations, which may be expected to increase our knowledge in a quite decisive way.

Prof. Herzog, to whom we owe so much fundamental work in the application of physical methods to investigation of high molecular structure, refers to a new effect in the light-scattering of diluted cellulose solutions. One seems to be able by his new methods to detect the merest traces of interaction between the dissolved particles.

Another suggestive paper on the optics of cellulose will be read by Dr. Preston, who has shown that the refractive index provides a good means for following the extension process of swollen cellulose fibres.

H. MARK

These papers, which are directly devoted to the structure questions of cellulose itself, will be followed by a couple of prominent communications as to the structure of cellulose-derivatives.

Dr. Sheppard, the famous chief of the Kodak laboratory, who unfortunately cannot appear personally, has sent a contribution on the structure of fibres and films of cellulose esters, in which he has applied the method of adsorption to determine the inner surface of these Xerogels. He concludes that it is highly probable that the micellar structure of these films is due to a molecular regrouping in the solution, and not to the persistence of the original micelles. Dr. Miles, in his paper concerning the molecular aggregation of cellulose, agrees with this point of view, and gives very convincing and interesting arguments for the suggestion that the original micelles are disturbed by the process of solution, but that there arises a certain regrouping in the solution, which is responsible for the technical behaviour of the investigated samples.

Dr. Trillat, whom we all know as an expert of the X-ray method, has investigated intra-micellar swelling by means of X-rays and ascertained that nitrocellulose forms molecular compounds with nearly every solvent—compounds which change during the evaporation of the solvent and give a series of intermediate states—an effect which had already been

pointed out by Hess, Katz, and Trogus.

Dr. Mathieu, who will represent in person the excellent French X-ray school, contributes a paper on the anisotropy of intramicellar swelling. He publishes a couple of excellent diagrams, which show very clearly that during the swelling of nitro-cellulose the planes perpendicular to the fibre axes remain practically unchanged, while the planes parallel to these axes very rapidly lose their regularity. This seems to be an interesting argument for the ideas of main valence chains, which may be taken as a basis of the present discussions on the structure of cellulose.

A very interesting point of the discussion will be the question of the shape of the fibre-molecules. We shall have highly interesting papers by Dr. Adam and by Dr. Hughes, both representative members of the British school of film-spreaders. This ingenious method has been worked out to an almost incredible degree of accuracy. Dr. Adam, especially, has studied the behaviour of spread molecules under the influence of very low lateral pressure and has derived from his results the reasonable assumption that the chains are not stiff, but that they are more or less flexible, so that their shape should not be taken as straight, but as more or less bent.

When we consider the great number of highly impressive contributions, we realise, firstly, that a lot of important new experimental material has been brought together, and then, that the question of the structure of cellulose and its derivatives is one of the most vivaciously worked and studied problems of present colloidal and organic chemistry. As another outstanding feature, we may point out that nearly every one of the present investigators has applied a different method for the study of the substance. There seems to me to be a certain amount of danger that the discussion may present difficulties of the nature which were present in ancient times during the construction of the tower of Babel, whose constructors did not succeed in reaching mutual agreement. But a danger which is known, ceases to be a danger, and as our discussions take place in the native country of the world-language, I am very sure that the conciliatory atmosphere of the English spirit will be the best guarantee for an effective and successful discussion.

## PART I.—GENERAL: RAW MATERIALS AND THEIR CONSTITUTION.

## THE FINE STRUCTURE AND THE MECHANICAL PROPERTIES OF FIBRES.

By H. Mark, Ludwigshafen/Rh.

Received 25th August, 1932.

The fact that we use cellulose compounds to such a large extent in the textile industry is due, not so much to the outstanding chemical behaviour of fibres consisting of this material, as to its unusual mechanical strength. If we look at Table I we notice that the strongest

TABLE I.—Tensile Strength of Cellulose and of some other Materials.

Material.			Ten in	sile Strengt n kg./mm.²
Cotton				28-44
Hemp				80-92
Ramie				70-80
Flax				60-110
Silk				35-44
Alumin	ium			10-40
Ebonite	•			2.5-5.5
Iron				34-50
Steel				50-160
Copper	•	•		20-50

fibres of cellulose or its compounds are superior to most metal wires. Only very good steel, tungsten, tantalum, and some other of the heavy metals are better than cellulose in respect of tensile strength.

This remarkable experimental fact leads us to investigate more thoroughly the mechanical behaviour of cellulose, and to try to find a connection between this important macroscopic peculiarity and the structure model, which is adopted to-day for the fine structure

of cellulose fibres by the majority of investigators.

It will not be necessary to repeat the features of this model in detail, as this has often been done; it will suffice to summarise those facts within our general knowledge on the fibre structure which we shall use in seeking a connection between the fine structure and the mechanical properties.<sup>1</sup>

Cellulose, for instance a certain cotton, which will be used to prepare rayon, consists of fibres with a diameter between I and 5 deniers or 80 and 400  $\mu^2$ , which has often a very irregular shape. These fibres are built up from the so-called *cellulose micelles*. They are bundles of long molecular chains, which are held closely together. We do not know exactly how many of these chains form one micelle, and it seems to depend to a very great extent upon the treatment which the sample has undergone, but we may estimate that one of these packets in native cotton or ramie fibre consists of about 40 or 60 of these chains. We

<sup>&</sup>lt;sup>1</sup> This model was worked out in the last five or six years by a series of successful investigators, especially by K. Freundenberg, W. N. Haworth, R. O. Herzog, K. H. Meyer, M. Polanyi, H. Staudinger, and G. L. Sponsler.

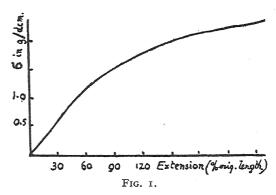
have reason to believe that the single chains of one special sheaf are not all exactly of the same length and structure; it seems, however, that the differences are not very great, so that we are entitled to speak of a certain average length and structure of these chains. The diameter of a micelle is between 50 and 70 Å, so that one single fibre contains about ten million micelles in its cross-section.

The chains themselves are built up of glucose units linked together by consecutive 1-4-glucosidic bonds; they were called *main valence chains*, and form the very backbone of the whole structure; their average length is not yet quite fixed, but it seems, one may assume for the most carefully treated natural samples, that the chains contain about 150 or 200 glucose-molecules, and that this number decreases very rapidly with every chemical treatment of the fibre. Glucose-units, main valence chains and micelles are the three essential building stones of cellulose fibres.

We have now to consider the question: What happens when one stretches a cellulose fibre?

Before we can attempt to answer this question we must know something about the orientation of the micelles in the original sample, because

it is clear that we must be informed about the initial situation if we wish to say something about the mechanism of the extension pro-When we concess. sider an artificial fibre, produced, for instance, by the cuprammonium process without any stretching during the spinning, we can study the orientation of the micelles with X-rays and we find that the



particles are orientated almost at random. This is proved by the X-ray patterns, which show the normal interference circles of a powder diagram. The strength of such a fibre is about 1.2 to 1.3 g/den. If we stretch it in the swollen state, so that the amount of stretching can be fairly large, there appear two striking facts:

(I) The fibre acquires an increased strength; and

(2) The micelles are orientated parallel to the direction of stretching. We get the same effect, if we do not extend in the presence of a swelling liquid, but if we stretch, for instance, a fibre of cellulose-acetate at higher temperatures, or even if we stretch a fibre only so slowly that its extension reaches an amount of 100 per cent. or more. The extension curves which correspond to such a process have a somewhat flat form, as is shown in Fig. 1.

We get the impression that the main process during the plastic deformation of cellulose is an orientation of the micelles. The effect produced by this micellar flow is very similar to the result of stretching a poly-crystalline metallic wire. Here one gets also an orientation of the elementary crystals, which is due to the glide-mechanism <sup>2</sup> of stretched crystallised bodies.

<sup>&</sup>lt;sup>2</sup> Cf. for instance M. Polanyi, Metallwirtschaft, 9, 563, 1930.

This formal analogy leads to the question: Is the mechanism of orientation in the case of micellar systems also of the same microscopic structure? Are there gliding planes in every single micelle, as in every single copper crystallite? Or is there another fundamental mechanism of deformation which leads to the orientation of the micelles in an extended fibre?

We cannot yet answer these questions definitely, but there is good reason to assume that the micelles remain intact during the deformation and that they flow as if they were soft, wormlike bundles.

The first fact which accords with this is the impossibility of detecting any decrease in the micellar size during the extension. If gliding planes had arisen one would expect that the angular breadth of the interference lines would be diminished. Nothing like this was ever observed.

In the case of normal polycrystalline deformation there are always the most densely packed planes, which act as gliding planes, and the most frequented directions, which are parallel to the direction of extension. In the case of micellar systems this rule does not hold, so that there is no reason to assume a very close connection between the elementary processes in both cases.

These results, and some others,<sup>3</sup> lead to the suggestion that the micelles are orientated as a whole, without being broken or torn during the real plastic extension. The question arises therefore whether we can give a quantitative interpretation of this effect, and the first task is to calculate how longish rods are orientated in a flowing medium. Eckling and Kratky <sup>4</sup> have treated this problem in a very interesting paper, and have shown that the amount of orientation is connected with the amount of extension by the formula

$$N(\alpha) = N_0 \frac{v^3}{(1 + (v^3 - 1)\sin^2 \alpha)^{3/2}} . (1)$$

 $N(\alpha)$  is the number of particles per unit angle, whose long axis form an angle  $\alpha$  with the direction of stretching,  $N_0$  is the number of particles per unit angle before the experiment; v is the amount of extension given by the equation

$$v=\frac{l}{l_0},$$

where  $l_0$  is initial length, and l the actual length of the sample.

We readily derive from (1) that, with increasing v the particles are more and more orientated, and that for a certain value of v we have a maximum of micelle axis parallel with the direction

$$\alpha = 0$$
.

Fig. 2 shows the amount of orientation for several values for  $\alpha$  in a diagram. The radius of the curves is for every point (i.e. for every  $\alpha$ ) proportional to the number of particles, whose axis form the angle  $\alpha$  with the direction of extension.

The relation (I) is in good qualitative agreement with the experiment, and some recent measurements show that also its quantitative content seems to be fairly good. Of course, one must not expect too close a conformity, because the formula calculates with independent rods put into a viscous medium, while the micelles of the fibre are in close contact

<sup>&</sup>lt;sup>3</sup> E.g. Eckling and Kratki, Naturw., 18, 461, 1930. <sup>4</sup> Loc. cit. <sup>3</sup> p. 464.

with one another. But in any case we may try to use the relation (I) for further attempts to get a quantitative interpretation of the extension curve of micellar systems.

We may start such an attempt from the following conception: in an unorientated fibre, as it is produced by spinning without extension, we have the micelles in a quite irregular distribution, without any preferred direction. The contact between them will not be very close; there are impurities and interstices which prevent the surfaces of the micelles from being attached or fixed very strongly together. If we

stretch the fibre, then the particles begin to move, they glide along and their internal contact becomes better and better. We will now assume that the tensile strength of a cellulose sample is proportional to the area of contact between the micelles, which increases during the progressive extension, and we will try to get an analytical expression for this area.

First, we consider only two micelles, which have a length of l and a diameter of b. When they are in the unstretched

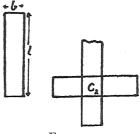


FIG. 2

state (Fig. 2) their contact surface is  $b^2$ , when they are orientated the corresponding surface is l.b. We should expect that at the beginning the tensile strength would be proportional to  $b^2$ , and at the end proportional to l.b. To get the value for every intermediate state, we have to calculate how the contact surface depends upon the angle  $\alpha$  between the axis of the two micelles. Neglecting certain factors concerned especially with the ends of the particles, we find that this surface is proportional to

$$f(\alpha, l, b) = \frac{b^2}{\sin \alpha + \frac{b}{l}} \quad . \qquad . \qquad . \qquad (2)$$

We shall now try to apply this formula to a great number of particles, and combine it with the relation (I). This equation gives us the number of particles per unit-angle, which form the angle  $\alpha$  with the direction of pull as a function of  $\alpha$  and v:—

$$N = N(\alpha, v); \qquad . \qquad . \qquad . \qquad (3)$$

on the other hand (2) expresses the contact surface for a definite position of two micelles as a function of  $\alpha$  and the axis ration,

$$\frac{b}{l} = \rho,$$

$$f = f(\alpha, \rho).$$

When we take the product  $N \cdot f$  and integrate it over all angles  $\alpha$ , then we get the whole internal contact surface between the micelles as a function of v and  $\rho:$ —

$$F = \int_{0}^{\pi/2} N(\alpha, v) \cdot f(\alpha, \rho) d\alpha = F(v, \rho).$$

This expression we must put proportional to the strength of our sample, which we obtain as a function of the amount of the extension v and of

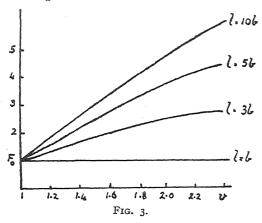
the axis ratio  $\rho$ . It is not very easy to evaluate the integral, and it is not possible at all to do it unless we neglect complicating factors. When we assume that the axis ratio  $\rho$  is small compared with unity, and that v is greater than unity, we arrive finally at the following expression for F:—

$$F \sim \frac{v^3}{1 - \rho + \rho v^3 - \rho^2 + \alpha \rho^2 v^6}.$$

We will neglect the members with  $\rho^2$  and consider only the formula,

$$F = F_0 \frac{v^3}{1 - \rho + \rho v^3}, \qquad . \tag{4}$$

which gives us the connection between the strength of the fibre, the



extension and the axis ratio of the micelles. Fig. shows 3 curves corresponding to the relation (4). see that they have the general type of extension curves of swollen cellulose derivatives. It may be of some importance for the technical application that the possibility of strengthening a fibre by extension is a function of  $\rho$ ; only samples which are characterised by a small

value of  $\rho$  can be strengthened at all. When we put

$$l=b$$
,

there is no increasing of F possible. This is a well-known fact in practice: only a carefully treated material, which contains long bundles, gives good and fast fibres.

This first attempt at a quantitative interpretation of the extension curve of a micellar system corresponds fairly well with our experimental knowledge, and shows that it might be useful to go a little deeper into the deformation mechanism of this kind of substance.

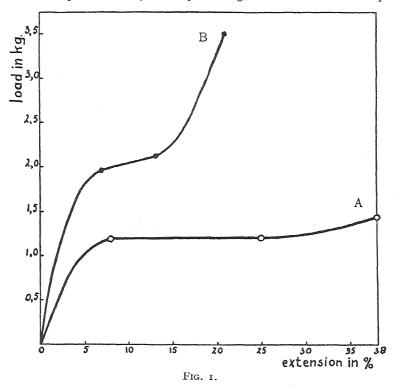
### GENERAL DISCUSSION.

**Professor Van Iterson** (Delft) said: From my own experience I can say that the extension curve of the non-ductile fibres (such as flax, ramie and hemp) has the form of the upper curve, marked l=10b in Fig. 3 in Professor Mark's paper. When stretching ductile fibres (such as cocoanut and kitul), extension curves such as that marked l=3b, or still more concave curves, are obtained. In the unstretched fibres of the first kind the micelles are orientated almost parallel to

the direction of stretching; in the latter ones under the same conditions, they are orientated oblique in regard to the fibre axis.<sup>1</sup>

We need not, however, suppose that the difference in form of these two kinds of extension curves has been caused by difference in the ratio  $b/l = \rho$ . It might be explained by the fact that the first kind of fibres only allow a small extension, the latter kind a large one. In other words the difference might be caused by the circumstance that when stretching non-ductile fibres we obtain only the first part of an extension curve, while with the ductile fibres a much greater part of that curve is produced.

On this point we may be in perfect agreement with the theory of



Professor Mark. I do not believe, however, that this theory can explain all the facts.

I reproduce two extension curves for the same film of cellophane (viscose-silk), one (B) found for strips cut in the direction of the machine, the other (A) for strips cut in the transverse direction. The latter (A) shows the character of the curve for a ductile fibre, the former (B) approaches that of a non-ductile one. Without doubt the difference between the curves is connected with the orientation of the micelles in the film. It is a well-known fact that they are orientated parallel to the surface of the film and moreover they possess an (imperfect) orientation in the machine direction.

<sup>&</sup>lt;sup>1</sup> See P. Sonntag, Die duktilen Pflanzenfasern, der Bau ihrer mechanischen Zellen und die etwaigen Ursachen der Duktilität, Flora **59**, 203-209, 1909.

Now, both curves show some important differences from the theoretical curves of Professor Mark. Firstly, curve A has a strictly straight and horizontal part, while curve B bends over more quickly than any of the curves of Professor Mark. Secondly, after the more or less horizontal part, both curves rise and become convex in regard to the extension axis.

This latter peculiarity is often to be observed in extension curves of fibres and films. It is even shown by Fig. 1 of Professor Mark's paper.2

As fas as I can see the very interesting theory of Professor Mark cannot explain the peculiarities mentioned here. I believe the theory needs some amplification. It has to take into account the difference between elastic and plastic deformation (both occurring when stretching fibres) and it has to seek an explanation of the bending upward of the last parts of the extension curves.

Mr. H. J. Woods (Leeds) (communicated): Although the curves given by Professor Mark are of the type to be expected in a theory of this sort, one or two suggestions with regard to the mathematical treatment might not be out of place. Since the curves are plotted for values of the extension greater than 100 per cent. (v = 2), the neglect of the term  $\rho^2 v^6$  is only justified when  $\rho$  is so small that  $64\rho^2$  is negligible compared with unity. This is not the case in any of the curves shown. If the approximation is not made, the shapes of the curves are considerably altered from those in the figure; for values of  $\rho$  not very different from I, F falls steadily as v increases, whilst for smaller values it first rises to a maximum and then falls to zero. In every case when  $\rho \geqslant 0.1$ , the maximum comes in the region of the diagram. It appears, therefore, that the approximations used are perhaps not sufficiently accurate. The derivation of the integral for F may also be improved by taking into account the possibility of a micelle whose orientation is  $\alpha$  being in contact with another whose orientation may have any value  $\theta$ . The integral would then read

$$F \propto \int_{0}^{\pi/2} N(\alpha, v) \int_{-\alpha}^{\alpha} N(\theta, v) f(\alpha - \theta, \rho) d\theta \cdot d\alpha,$$

since the number of pairs of micelles in contact whose orientations lie in the ranges  $d\alpha$  and  $d\theta$  about the values  $\alpha$  and  $\theta$  is proportional to  $N(\alpha)d\alpha$ .  $N(\theta)d\theta$ , and their area of contact is  $f(\alpha-\theta,\rho)$ .

**Professor H. Mark** (Wien) said: I agree absolutely with what Mr. Woods has said. Indeed, I pointed out in my paper, that only a first rough approximation of a quantitative treatment of the extension of micellar systems was attempted; it will be necessary to improve it in several directions. There are different difficulties, which arise during the calculation; one only need be pointed out: it is assumed that the micelles are stiff sticks—an idea which may be justified, but which may be also quite wrong; it could be also imagined, that the micelles are soft wormlike bundles, which can be bent to a rather considerable amount. Then the calculation would be very complicated. When one wants to proceed in the direction indicated it seems to be best to work out very carefully the connection between the extension curve

<sup>&</sup>lt;sup>2</sup> See also the book of Clément et Rivière, La Cellulose, 1920. examples are further to be found in J. B. Speakman, "The Intracellular Structure of the Wool Fibre," J. Text. Inst., 18, 431-453, 1927, where is shown that wool in air of 100 per cent. relative moisture has an extension curve of the form A, and wool in drier air gives curves of the form B.

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and the length of the micelles. When one has a large experimental material on this subject, then it will be possible to improve the mathematical expression for the extension so far as one can do it by theoretical considerations.

**Professor P. P. von Weimarn** (Kobe, Japan) (communicated): In connection with the very interesting paper of Professor H. Mark I should like to point out that the influence of the degree of orientation of the disperse particles upon the tensile strength of the thread can be especially easily demonstrated on the silk threads which are obtained by coagulation from solutions of natural silk, in concentrated aqueous solutions of neutral salts.

By repeated stretchings and by rubbing the thread possessing minimum orientation of disperse particles, in the longitudinal direction (e.g. with two fingers), there is obtained a progressively increasing orientation of the disperse particles and the tensile strength of the thread progressively increases (e.g., from 10 kgs./mm.² to 30 kgs./mm.²). As a result of the orientation of the disperse particles in the surface layer, the thread acquires the beautiful lustre which is peculiar to the threads of natural silk.

Jellies of natural silk with minimum orientation of their disperse particles which I have obtained, become transformed, on drying, into a perfectly solid glass which can be broken only with a knife and hammer. This silk glass is transparent in a layer of I to I·5 cm.; in transmitted light it looks yellow or brownish-yellow.

The methods for obtaining threads, jellies and glass from solutions of natural silk in concentrated aqueous solutions of neutral salts, and certain numerical data concerning the influence of the degree of orientation of the disperse particles in threads upon their tensile strength, may be found in my paper: "Dispergation and Aggregation of Natural Silk in Aqueous Solutions of Neutral Salts," published in J. Alexander's Colloid Chemistry, Vol. IV, pp. 363-398. New York (1932).

Professor Mark (Wien), in reply, said: It is very interesting that, according to Professor Weimarn's communication, the orientation of protein chains can be reached in such a simple and perfect manner, because it is not so easy to obtain a good orientation of cellulose chains. The reason for the different behaviour might be found in the fact that the protein particles are very flexible while the cellulose micelles are more rigid, an assumption which is in good agreement with our general knowledge on X-ray patterns of stretched and unstretched fibres. Rubber chains are still more flexible; they only remain in the orientated state as long as the tension is applied on them; when the external stress is removed, they immediately obtain their bent or helicoidal shape.

In reply to Professor von Weimarn, Professor Mark wrote: The difference between the two curves of Fig. 1 is very interesting. It cannot be explained by the theory put forward, because in the case of normal cellophan the original sample does not consist of quite unorientated cellulose. It is well known from practice and from the X-ray investigation of cellophan, that the technical product shows already a certain orientation of the micelles. The formulas and curves, which were given in the contribution, refer only to samples, which are originally quite unorientated. I think, that the difference in the behaviour between technical cellophan and the samples, which we have used, may be explained in this way.

### THE MOLECULAR STRUCTURE OF POLY-SACCHARIDES.

By W. N. HAWORTH AND E. L. HIRST.

Received 4th August, 1932.

Following upon the definite allocation of ring structures to the monosaccharides and disaccharides rapid progress has been made in the investigation of the molecular structure of the polysaccharides and many of the problems connected therewith may be regarded as having reached solution. It is now held fairly generally that the polysaccharides are constituted on the basis of long chains of monosaccharide residues united by glycosidic links. On this view the molecule may terminate in two end groups or alternatively may exist as an endless loop in which all the monosaccharide residues are alike and show no singular property in any one of them. In certain cases, notably for cellulose derivatives, estimates have been made by physical methods of the size of the macromolecules, but hitherto the problem of the existence or non-existence of terminal groups has remained unsolved. It has now been found that by a purely chemical method of attack a decision can be reached as to the presence of terminal groups whilst at the same time an estimate can be made of the molecular magnitude. This is accomplished by a study of the hydrolysis products obtained from a highly purified methylated derivative of the polysaccharide. In the event of a loop structure being present in the polysaccharide all the methylated monosaccharide residues would give rise after hydrolysis to the same methylated monose. Taking cellulose as example, a loop structure would result in the isolation of 2:3:6-trimethyl glucose only, whereas if a terminated chain is present one of the terminal groups would give rise to a molecule of tetramethyl glucose. From a knowledge of the proportion of the latter substance in the hydrolysis products the chain length can be calculated. method is of general application and in the following paragraphs a summary is given of the results obtained by applying it to cellulose and cello-dextrins (Haworth and Machemer), to the amylose and amylopectin fractions of potato starch (Hirst, Plant and Wilkinson), to glycogen (Haworth and Percival) and to inulin (Haworth, Hirst and Percival).

Cellulose.—The traditional view that the glucose residues in cellulose are mutually linked as in the disaccharide cellobiose (4-\beta-glucopyranosido-glucopyranose) is demanded by the chemical evidence and derives further sanction from the interpretation of the X-ray data given by Sponsler, Meyer, Mark and others. The thread-like macromolecule of cellulose is to be pictured as a straight chain of glucopyranose units linked together through positions I and 4. Hydrolysis of a sample of methylated cellulose which had been prepared from cellulose under stringently controlled conditions and the essential homogeneity of which had been rigidly tested, gave tetramethyl glucopyranose to the extent of 0-6 per cent. by weight of the material subjected to hydrolysis. Control experiments have shown that under the conditions adopted the separation of tetramethyl glucose from trimethyl glucose can be effected

quantitatively and the conclusion is reached that cellulose consists of thread-molecules which terminate and are not looped and that the methylated cellulose examined had a chain length of not fewer than 100 and not more than 200 glucose units, corresponding to a molecular weight of 20,000-40,000. The methyl derivative was prepared from cellulose by chemical methods which may have involved some degree of scission of the large molecules (without formation of break-down products of small molecular magnitude) and the size of the macro-molecule in native cellulose may be somewhat larger. It seems, however, that no vital point is involved here inasmuch as the order of magnitude of the molecular weight is to be regarded as in good agreement with the determinations of Staudinger based on viscosity measurements. Cellulose is to be considered as an extraordinarily large assembly of  $\beta$ -glucopyranose units linked through positions I and 4 and continued by reason of the stereochemical arrangement of the primary valency bonds as a straight chain of six-atom ring units. The lower mean average chainlength is of the order of 100-200 glucose units and the colloidal properties of cellulose are readily understandable on this structural conception.

Application of this method of enquiry to cellodextrins has yielded evidence concerning the average chain length of these break-down products of cellulose and has at the same time provided evidence both of the accuracy of the method itself and of the fact that methylation of polysaccharides under suitably controlled conditions can be carried out with little or no break down of the macromolecules concerned. An independent assay of the chain length of the cellodextrins can be made by the method of Bergmann and Machemer (iodine numbers) and the values so obtained are in excellent agreement with those found by hydro lysing the methylated derivatives and estimating the amount of tetramethyl glucose in the products.

ramethyl glucose + methyl alcohol Methylated cellulose (x = 100-200).

Starch.—Maltose (4- $\alpha$ -glucopyranosido-glucopyranose) is related to starch in the same way as cellobiose is to cellulose, and the starch molecule consists of a succession of  $\alpha$ -glucopyranose units linked through carbon atoms I and 4. The position here is not so simple as with cellulose in that  $\alpha$ -glucosidic links do not lend themselves to the formation of straight molecules. Furthermore, the starch granule is not homogeneous and is generally held to consist of a soluble portion (amylose) and a less soluble portion (amylopectin), the latter being responsible for the paste-forming properties. The relationship between the two modifications has been obscure and at one time the work of Samec seemed to

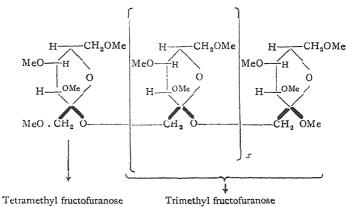
indicate a connection between the phosphorus content and paste formation. This view is not, however, entirely satisfactory, since it is possible to prepare amylose fractions which retain the full complement of phosphorus. It has been observed that amylopectin reacts chemically as if it were composed entirely of amylose, whilst amylose cannot be kept as such but retrogrades through a continuous range of intermediate stages to the amylopectin condition. These results can be readily explained on the views which emerge, concerning the nature of starch, from a study of the methylated derivatives of amylose and amylopectin. The relationship between these two methylated starch fractions is simpler than had been anticipated inasmuch as each has a chain length of about 24 glucose units. The chains are not endless but terminate in a glucose residue which gives rise to tetramethyl glucopyranose. No evidence of decomposition during the methylation was observed and it was proved by control experiments that the presence of break-down products of low molecular weight could easily have been detected by the methods of fractionation to which the methylated derivatives were subjected before hydrolysis. We conclude that amylopectin and amylose consist of macro-molecules containing about 24-30 α-glucopyranose units in the chain and that they differ in the condition of aggregation and hydration, the tendency towards aggregation and interlocking of molecules being occasioned by the stereochemical conformation of the macromolecules produced in consequence of the α-glucosidic linkages. The colloidal properties of starch and the micellar character of starch solutions are readily understood on this view. These results

were obtained with potato starch. Other investigations are in progress to determine whether this chain length is found in other starches also or whether it is characteristic of this particular variety of starch.

Glycogen.—This polysaccharide closely resembles starch in its chemical properties and consists of chains of  $\alpha$ -glucopyranose units linked as in maltose. Examination of a highly purified methylated derivative has revealed that these chains terminate like those of starch but have a mean average length of only 12 glucose units. This value is about half that found for starch, and it is significant that glycogen does not possess the property of retrograding to an insoluble modification. It may be suggested that this phenomenon is micellar in origin and that the requisite aggregation and interlocking of the macromolecules do not take place unless the latter have a certain minimum chain length.

Glycogen and starch are almost completely non-reducing and on account of this fact difficulties arise concerning the nature of the second terminal group, which on the ordinary view would be held to be a reducing group. The reducing power may perhaps be masked owing to the micellar character of the solutions, but the alternative view that this group has undergone some modification which renders it stable to alkali and oxidising agents is also being considered.

Inulin.—All the above-mentioned polysaccharides have the common feature that on hydrolysis their methylated derivatives yield the stable substances 2:3:6-trimethyl glucose and tetramethyl glucopyranose. Methylated inulin, on the other hand, is composed of labile methylated



Tetramethyl fructofuranose Trimethyl fructofuranose Methylated inulin (x = 30).

fructofuranose units and gives rise to methylated fructofuranose derivatives on hydrolysis. It has been found, however, that the same method of enquiry can be used in this case also. By suitable methods of hydrolysis the decomposition of the fructofuranose derivatives to methoxymethyl furfural can be reduced to negligible proportions and it is then found that a highly purified and rigidly fractionated methylated inulin gives, in addition to 3:4:6-trimethyl fructofuranose, 1:3:4:6tetramethyl fructofuranose to the extent of 3.7 per cent. It follows that inulin is composed of a chain of fructofuranose units linked through positions I and 2, the number of units in the chain being on the average about 30. Since the purest samples of inulin are slightly reducing it is highly probable that the other terminal group in the inulin macromolecule is a reducing fructofuranose unit. The molecular weight of inulin is about 5000, a value which is in good agreement with estimates of the molecular weight which had been obtained previously (Drew and Haworth) from ebullioscopic measurements with freshly prepared solutions of inulin. Just as cellulose, starch, and glycogen break down to their constituent bioses, so inulin can be degraded to a di-hexose unit which is isolated, in yield of 50 per cent., as a hexa-acetyl difructofuranose anhydride, and finally as  $C_{12}H_{20}O_{10}$ .

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## VISCOSITY INVESTIGATIONS FOR THE EXAMINATION OF THE CONSTITUTION OF NATURAL PRODUCTS OF HIGH MOLECULAR WEIGHT AND OF RUBBER AND CELLULOSE.

By H. STAUDINGER, Freiburg i. Br.

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### The Constitution of Compounds of High Molecular Weight.

One of the most striking properties of natural substances of high molecular weight is the high viscosity of their solutions. Even one per cent. solutions of rubber in benzene or of nitrocellulose in acetone have a very high viscosity, this being at least a hundred times as great as that of the solvents, while I to 2 per cent. solutions in the same solvents of similarly constituted substances of low molecular weight have a low viscosity. The investigation of the cause of this high viscosity has occupied chemists and colloid workers repeatedly during the last decades.

Highly viscous solutions similar to those of the natural substances of high molecular weight, the structure of which was previously unknown, are given by a series of substances of well-known structure, e.g., by the soaps in water. With these soap solutions it was possible to show that the salts of the higher fatty acids do not pass into solution as normal salts, but that a number of simple salt molecules collect together to form larger colloid particles. The latter were termed micelles. The high viscosity of soap solutions is connected with the formation of these micelles, because solutions of soap in alcohols, in which the soap molecules are in the normal state, have a low viscosity.

After the work of Krafft, Zsigmondy, McBain and others had led to the recognition of the colloidal nature of soap solutions, it seemed reasonable to ascribe a similar structure to the colloid particles in solutions of substances of high molecular weight, as the solutions of these products exhibited phenomena similar in many respects to those of the soap solutions. During the last decades it has therefore been frequently assumed that the colloid particles in solutions of substances of high molecular weight possessed a micellar structure, and it was believed that the behaviour of the colloidal solution and its high viscosity could be explained by means of special solvation phenomena occurring with these colloid particles. This view has been expressed especially by McBain.¹ Later on it was developed by K. H. Meyer ² into a special micelle theory of substances of high molecular weight.

The chemical investigation of substances of high molecular weight had, however, in the meanwhile arrived at the result 3 that these sub-

<sup>&</sup>lt;sup>1</sup> Cf. McBain, J. Physical Chem., 30, 239, 1926.

<sup>&</sup>lt;sup>2</sup> Cf. K. H. Meyer, Z. angew. Chem., 41, 935, 1928. <sup>3</sup> Cf. the summarising paper by H. Staudinger: The chemistry of substances of high molecular weight discussed on the Kékulé theory of structure, Ber., 59, 3019, 1926.

stances consist of very long molecules, in which a hundred or more single molecules are bound by means of main valencies into chains, and it was furthermore proved that these molecules, which were termed fibre molecules (Fadenmoleküle), dissolve normally, like the molecules of substances of low molecular weight. The structure of substances of high molecular weight was first revealed in the case of some synthetic products, such as the polyoxymethylenes and the polystyrenes, where specially simple conditions prevail. The results could be extended later also to natural products, such as rubber and cellulose.4 All these substances when dissolved are molecularly dispersed. The properties of their solutions can, therefore, not result from a micellar structure of the colloid particles and special solvation phenomena occurring with them, but the colloidal nature of the solutions is connected with the size and special shape of the molecules. The investigation of this connection and the results of viscosity experiments provided confirmation for the results found chemically. The behaviour of long molecules in solution is in agreement with their behaviour in the solid form of the substances. These viscosity experiments are described below.

### Viscosity Experiments on Solutions of Substances of Low Molecular Weight.

In order to investigate the general connection between the viscosity of a solution and the shape of the dissolved molecules, a series of solutions of substances of low molecular weight and with approximately spherical molecules were examined. Afterwards substances with fibre or chain form molecules were used.

The lower sugars provide, such as the monoses and bioses, examples of approximately spherical molecules, and also substances like phenylacetic acid and diphenylacetic acid and some of the lower acids such as malonic acid, succinic acid and glutaric acid. If dilute solutions of these substances are examined, the specific viscosity of solutions of equal concentrations is found to be approximately constant, *i.e.*, in the case of substances similar in structure, the specific viscosity of equally concentrated solutions is independent of the molecular weight, that is, of the number of particles in the solution. Einstein's rule is therefore valid here: the viscosity is independent of the degree of dispersion and depends only on the volume of the dissolved phase, *i.e.*, only on the concentration.<sup>5</sup>

The behaviour of substances with long chain molecules is different. X-ray investigations of the Bragg school, principally those of Müller and Shearer, have shown that the molecules of normal paraffins, normal fatty acid esters and fatty acids have, in the crystalline state, the form of elongated chains. These molecules also possess the same shape in solution, as can be readily understood, since the ready crystallisation of these substances would not be possible if their molecules when in solution were, for instance, coiled up into spirals. The elongated form of

<sup>&</sup>lt;sup>4</sup> Cf. H. Staudinger: "Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose." (The organic compounds of high molecular weight, rubber and cellulose.) Published by Springer, Berlin, 1932.

<sup>5</sup> H. Staudinger and W. Heuer, Ber., 63, 230, 1930.

<sup>&</sup>lt;sup>6</sup> Cf. A. Müller, J. Chem. Soc., 123, 2043, 1923: Müller and G. Shearer, J. Chem. Soc., 123, 3156, 1923; Shearer, J. Chem. Soc., 123, 3152, 1923; Müller and Shearer, J. Chem. Soc., 123, 3152, 1923; Müller and Shearer, J. Chem. Soc., 123, 3159, 1923; Müller, Proc. Roy. Soc., 114A, 542, 1927; O. L. Sponsler, and W. H. Dore, Colloid Symposium Monograph, 174, 1926; cf. translation of this in Cellulosechemie, 11, 186, 1930.

the molecules in solution is also shown by the experiments of Langmuir and Adam <sup>7</sup> on surface films as well as by those of R. Signer <sup>8</sup> on the double refraction. In the case of substances with molecules having such a long chain form, the viscosity of equally concentrated solutions is not constant, but is proportional to the molecular weight of the substance. As in the case of these long chain molecules the molecular weight is proportional to the length of the chain, the viscosity of the solution increases with the length of the molecule; for these substances, therefore, Einstein's rule no longer holds, in contradistinction to substances with spherical molecules.

In order to find a law here to connect the viscosity and the molecular weight, the *specific* viscosities of solutions, and not, as formerly, their relative viscosities, are compared. By specific viscosity is here understood the increase in viscosity which is produced in a solvent by a dissolved substance. The specific viscosity is therefore  $\eta_r - 1$ . Between the specific viscosity,  $\eta_{\rm sp.}$ , of equally concentrated solutions and the molecular weight of substances with long fibre molecules we have the following simple relation:  $\eta_{\rm sp.}/c = K_m$ . M, where c is the concentration of a primary  $^9$  molar solution.  $^{10}$ 

As M is proportional to the length of the chain and as the specific viscosity of the solution increases with the length of the chain, this formula can be written:  $\eta_{\rm sp.}/c = K_t \cdot L$ , where L is the length of the chain in A.

If solutions of paraffin derivatives, 11 fatty acids and fatty acid esters 12 be now examined, the viscosity of solutions of these substances is likewise composed of the viscosities of the paraffin chains and of the oxygen atoms in the chains. The specific viscosity of a primary molar, i.e., 1.4 per cent. solution is accordingly to be expressed thus:  $\eta_{\rm sp.}$  (1.4 per cent.) =  $n \times y + x$ , where n is the number of carbon atoms in the chain, i.e., of the CH2-groups, y the viscosity value for one chain carbon atom and x the viscosity value for the oxygen atom. The viscosity value, y, for one chain carbon atom is approximately the same in the different substances. This is due to the fact that the relationship between the viscosity and the chain length in the different homologous series can be represented graphically by mutually parallel straight lines (Fig. 1). Using this graphical method of representation, the viscosity value, x, for the foreign group in the molecule can be determined as the intercept on the ordinate. The abscissa represents the number of carbon atoms in the molecule. In the case of the fatty acids, however, it is not the number of carbon atoms in the normal molecule that is used for the abscissa but the number of carbon atoms in the co-ordinated molecule, for the acid particles are present in solution, just as in the crystalline

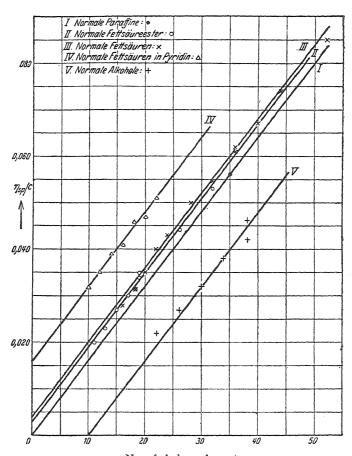
<sup>&</sup>lt;sup>7</sup> I. Langmuir, J. Amer. Chem. Soc., 38, 2221, 1916; 39, 1848, 1917; N. K. Adam, The Physics and Chemistry of Surfaces, Clarendon Press, 1930; Kolloid-Zeitschr., 57, 125, 1931.

<sup>&</sup>lt;sup>8</sup> Z. physikal. Chem., 150A, 257, 1930.
<sup>9</sup> By the primary molecule of a long chain molecule is here designated that structural unit which, when regularly linked end to end, builds up the long chain molecule. The primary molecules of the normal paraffins and paraffin derivatives is the CH<sub>2</sub> group; a primary molar solution of such substances has, therefore, a concentration of 1.4 per cent.

H. Staudinger and W. Heuer, Ber., 63, 222, 1930.
 H. Staudinger and R. Nodsu, Ber., 63, 721, 1930.

<sup>12</sup> H. Staudinger and E. Ochiai, Z. physikal. Chem., 158A, 35, 1931.

state, not as the normal molecules but as the co-ordinated and elongated double molecules :--



---- No. of chain carbon atoms.

- Normal paraffins.
   Normal fatty acid esters.
- III. Normal fatty acids.
- IV. Normal fatty acids in pyridine.
  V. Normal alcohols.

Fig. 1.

In the case of the normal alcohols a negative value is obtained for x, i.e., for the foreign group, because a mixture of normal and co-ordinated molecules is present in these solutions. The degree of dissociation of these co-ordinated molecules can thus be determined by means of viscosity measurements.

Such simple relationships between viscosity and molecular weight are, however, only found in the case of solutions of homopolar compounds in indifferent solvents, for only then the long chain molecules are surrounded by a monomolecular layer of solvent molecules. A further essential condition for the validity of these laws is that the measurement should be performed in dilute solution, so that the long chain molecules may be isolated from one another. Furthermore, only viscosity measurements at the same temperature can be compared, for, as the temperature increases, the distances between the molecules all change, also, therefore, the distances between the dissolved molecules and the solvent molecules, which is accompanied by a change in the specific viscosity. The specific viscosity, therefore, decreases as the temperature increases, just as the absolute viscosity of liquids decreases as the temperature increases.

Far more complicated conditions prevail in solutions of heteropolar substances, *i.e.*, in solutions of salts of organic acids and bases. Here, resembling the case of solutions of electrolytes of low molecular weight, the formation of swarms occurs due to one ion attaching others to itself. This production of polyvalent long chain ions manifests itself in a considerable increase in the viscosity. Thus mathematical relationships between the viscosity and the molecular weight of heteropolar molecular colloids result only under special conditions.<sup>13</sup>, <sup>14</sup>

## Viscosity Experiments on Solutions of Substances of High Molecular Weight.

Thus it can be deduced, from the viscosity phenomena presented by solutions of simple paraffins and paraffin derivatives, that laws for the relationship between the viscosity and the molecular weight can only be found when homopolar substances are present in solution in the form of long fibre molecules. The relationship between viscosity and molecular weight was therefore first investigated in the case of highly polymeric hydrocarbons, such as the polystyrenes, esters, the polyvinylacetates, the polyoxymethylenes and ethers, the choice falling on such substances of high molecular weight for which the molecular weight could be determined by the cryoscopic method and therefore had values lying between 1000 and 10,000. The degree of polymerisation of these products varied, according to the size of the primary molecule, between 10 and 300. Substances with these relatively low molecular weights do not yet show, when in solution, the characteristic properties of the natural products of high molecular weight, such as rubber or cellulose. These compounds, forming a transitional group between substances with small, discrete molecules and the products with a really high molecular weight and providing the connecting link between the two, were termed hemicolloids. These hemicolloids can

<sup>&</sup>lt;sup>13</sup> An additional complication in the case of acids of high molecular weight results from the formation of micelles, which is due to the fact that, with the soaps for instance, the fatty acid ions collect together, because of their insolubility, so that only the hydrophyllic ions are present on the surface of these micelles. Naturally, in the presence of such micelles in the solution, relationships between the viscosity and the molecular weight of the solute cannot be found.

 $<sup>^{14}</sup>$  Cf. " Die hochmolekularen organischen Verbindungen," publ., Springer, 1932, P. 333·  $^{15}$  H. Staudinger, Ber., 59, 3031, 1926.

be obtained by the polymerisation of unsaturated compounds of low molecular weight, for instance, by the polymerisation, either by the addition of catalysts or at higher temperatures, of styrene, ethylene oxide or vinyl acetate. Hemicolloidal representatives of the natural products of high molecular weight, such as rubber and cellulose, which consist of very long chain molecules, are obtained through their degradation, e.g., by cracking at higher temperatures.

The relationship which holds between the viscosity of the solution of these hemicolloidal products and their molecular weight is the same as that existing in the case of simple substances of low molecular weight. The viscosity of equally concentrated solutions accordingly increases proportionally to the molecular weight and the formula  $\eta_{\rm sp.}/c = K_m \times M$  holds here too. The constant,  $K_m$ , for the individual polymerised products have been determined subsequently, as with the help of these  $K_m$  constants it is possible to determine the molecular weight of a substance with long chain molecules by means of a simple viscosity measurement on a dilute solution. The value of the constant,  $K_m$ , is the same for one and the same polymerhomologous series. <sup>16</sup>

### Viscosity Laws for Solutions of Long Fibre Molecules.

From what has been said it follows that viscosity measurements play a special part in the elucidation of the constitution of compounds with a high molecular weight, as the shape and size of the colloid particles can be determined by means of such investigations.

Once the constants,  $K_m$ , for the different series were known, a comparison of them revealed also a general relationship existing between the different polymerhomologous hydrocarbon series, namely: equally concentrated solutions of such hydrocarbons as are built up of long fibre molecules contain molecules of the same length whenever the specific viscosity of the solutions is the same. The particular structure, therefore, of the long chain molecules as well as their chemical behaviour, which is naturally different in the different polymerhomologous series, do not enter into the question of the viscosity; only the length and number of the molecules do so.

These results are arrived at as follows. The viscosity of a 1.4 per cent. solution is calculated from various viscosity measurements performed on any suitable hydrocarbons and then the chain length, or number of molecules in the chain, is evaluated, where

No. of members in chain (Length of chain) =  $\frac{\text{Molecular weight.}}{\text{Chain equivalent weight}}$ 

The chain equivalent weight of a compound is the average weight per carbon atom in the chain of the molecule. In the case of polymerised compounds, it is obtained by the division of the weight of the primary molecule by the number of chain carbon atoms, *i.e.*, of the carbon atoms which actually lengthen the chain, in the primary

molecule. For instance with rubber it is  $\frac{68}{4} = 17$ .

If one now calculates the specific viscosity of the various compounds which have the same number (say 1000) of chain carbon atoms in the molecule, *i.e.*, in which the long chain molecules have the same length,

Cf. e.g., H. Staudinger, Z. physikal. Chem., 153A, 391, 1931.
 H. Staudinger, Ber., 65, 267, 1932; Helv. chim. acta, 15, 213, 1932.

then the specific viscosity of solutions of the same percentage strength

is approximately constant (column 8, Table I.).

The specific viscosity in 1.4 per cent. solution of hydrocarbons with 1000 carbon atoms in the chain is therefore on the average 1.2. The specific viscosity, in 1.4 per cent. solution, of a hydrocarbon with nmembers to the chain is accordingly given by:

$$\eta_{\text{sp. (r-4 per cent.)}} = \text{I-2} \times \text{IO}^{-3} \times n.$$

From this the specific viscosity of solutions normal with respect to the chain equivalent weight can be calculated:—

Now the product of the chain equivalent weight and n is the molecular weight, M, of the hydrocarbon. Therefore we have

$$\eta_{\text{sp. (equ.)}}^* = \frac{1.2 \times 10^{-3}}{14} \times M = 0.85 \times 10^{-4} \times M.$$

TABLE I.

	Molecular Weight.	η <sub>sp.</sub> Found.†	Per Cent. Content of Solution.	nsp. Cal- culated for a 1.4 Per Cent. Solution.	Chain Equi- valent Weight.	Length of Chain.	nsp. of 1'4 per cent. Solution when Chain has 1000 Members.
Paraffin <sup>18</sup> Polyprane <sup>19</sup> Polyprene <sup>20</sup> Polyisobutylene <sup>21</sup> . Polystyrene <sup>22</sup> . Polyindene <sup>23</sup> .	492 5500 6400 1500 7600 6000	0.043 0.41 0.507 0.13 0.353 0.59	1.4 1.75 1.7 2.8 2.6 5.8	0.043 0.328 0.418 0.065 0.190 0.143	14 17.5 17 28 52 58	35 314 376 54 146	1.23 1.04 1.11 1.20 1.30 24 1.39 24

Therefore an additional simple relation results: When normal with respect to the chain equivalent weight, solutions of polymeric hydrocarbons having the same molecular weight have the same specific viscosity, independent of the structure of the molecules.

The molecular weight of, for instance, rubber can therefore be deduced from viscosity determinations by the use of the general viscosity laws without having determined the particular  $K_m$ -constant of rubber.

† The measurements were performed in tetralin or benzene. 18 Z. physikal. Chem., 158A, 35, 1931.

<sup>\*</sup>  $\eta_{SP. (equ.)}$  stands for the specific viscosity of a solution normal with respect to the chain equivalent weight.

<sup>&</sup>lt;sup>19</sup> Helv. chim. acta, 13, 1348, 1930.

<sup>20</sup> Ber., 63, 734, 1930.

<sup>&</sup>lt;sup>21</sup> Helv. chim. acta, 13, 1379, 1930.

<sup>22</sup> Ber., 63, 232, 1930.

<sup>&</sup>lt;sup>28</sup> Helv. chim. acta, 12, 939, 1929.

<sup>&</sup>lt;sup>24</sup> As polystyrenes and polyindenes are richer in carbon than the polypranes, the viscosity of a 1.4 per cent. solution is in their case a little higher than with the compounds poorer in carbon.

These viscosity laws also hold for compounds containing oxygen, that is for those in which oxygen atoms 25 may replace carbon atoms as members of the chain, as is the case, for instance, with the polyoxymethylenes.26, 27

### Viscosity Investigations on Cellulose and Cellulose Derivatives.

These viscosity laws are apparently not valid for cellulose and cellulose derivatives, for the viscosities of solutions of cellulose in Schweizer's reagent or of triacetyl cellulose in m-cresol are far higher than those calculated on the basis of the viscosity laws.28 A triacetyl cellulose solution with a chain formed of 100 atoms has a specific viscosity in a 1.4 per cent. solution of 3 instead of 1.2. This abnormal behaviour of cellulose and its derivatives is, however, due to the fact that it is not a question of simple long chain molecules with a string-like arrangement of the atoms, but that, according to the Haworth formula for cellulose, 6-membered rings are the fundamental molecules present as chain members, corresponding to the following formula:—

These 6-membered rings require an increase in viscosity, which increase is found with all compounds with 6-membered rings. If, for instance, derivatives of benzene, cyclohexane or of piperidine are prepared so that a 6-membered ring is attached to a long and extended chain, as in the stearic acid ester of phenol or cyclohexanol or as in the piperides of acids, then the viscosity of all these compounds is greater by a definite, approximately constant amount, than that calculated for molecules of this length. This increment in the viscosity due to a 6-membered ring has, in I-4 per cent. solution, the general value  $^{29}$  of  $9 \times 10^{-3}$ . If this increment be now taken into account, a value for the viscosity of the celluloses and cellulose acetates is obtained which agrees with that found experimentally, as is shown by the following calculation. A cellulose acetate with 1000 atoms forming the chain of the molecule has a degree of polymerisation of 200; the same number of 6-membered rings is therefore present. An increment of  $200 \times 9 \times 10^{-3} = 1.8$  is calculated for these 6-membered rings. This viscosity value is to be added to 1.2, where 1.2 is the viscosity value calculated for a molecule with 1000 carbon atoms in the chain. A specific viscosity of 3.0 is therefore obtained for a 1.4 per cent. solution of a triacetyl cellulose with 1000 carbon atoms in the chain, Haworth's pyran structure for cellulose being taken as a basis and the increments for the 6-membered rings being taken into account. The value found by viscosity determinations

<sup>25</sup> The slight difference in the weight per chain member for oxygen (16) and

the CH<sub>2</sub> group (14) need not be taken into account.

<sup>26</sup> Cf. "Die hochmolekularen organischen Verbindungen," p. 224.

<sup>27</sup> For the behaviour of the polyethylene oxides, cf. H. Staudinger and H. Lohmann, in "Die hochmolekularen organischen Verbindungen," Springer, Berlin,

<sup>1932.

28</sup> Cf. "Die hochmolekularen organischen Verbindungen," p. 446. <sup>29</sup> Experiments performed by R. Bauer.

was 3.05. Thus the constant  $K_m$  for cellulose, which was determined by investigating the polymerhomologous series of cellulose decomposition products, can nowadays be calculated very simply by combining the viscosity measurements of long chain molecules and of derivatives of 6-membered rings.

### The Molecular Weight of Rubber, Cellulose and Other Products of High Molecular Weight.

The validity of the viscosity laws has at present been proved experimentally up to a molecular weight of 10,000 by the investigation of substances of low molecular weight and of different polymerhomologous series of hemicolloids. The viscosity laws therefore hold for chain molecules having a length ranging from 20Å. up to 300-500Å. If these viscosity laws be now applied, in order to arrive by means of viscosity measurements on dilute solutions at the molecular weight of rubber, cellulose and other highly polymeric compounds, the results collected in the following table are obtained:-

Substance.	η <sub>sp.</sub>	Concentration in Primary Mols.	Con- tent Per Cent.	$\frac{\eta_{\text{sp.}}}{c}$ .	K <sub>m</sub> .	Average Molecular Weight.	Average Degree of Poly- merisa- tion "a".	No. of Atoms Forming Chain.	Length of Chain in Å.
Polystyrene . Polyvinylace-	0.11	0.001	0.01	110	1.8×10-	600,000	6000	12,000	15,000
tate	0.26	0.0125	0.108	20.8	2.6 ,,	80,000	900	1,800	2,200
Caoutchouc .	0.380		0.068	38∙0	3.0 ,,	125,000	1800	7,200	8,100
Balata .	0.386	0.025	0.17	15.0	3.0 ,,	50,000	750	3,000	
Cellulose .	0.302	0.0025	0.040	121.4	10 ,,	120,000	750	3,800	3,900
Triacetylcellu- lose	0.284	0.0025	0.072	113.6	II ,,	103,000	360	1,800	1,900

TABLE II.

The conclusion is therefore reached that rubber and cellulose have molecules which may be about 1000 times longer in one dimension than in the other two. These molecules must have the shape, to use an illustration, of long, thin sticks, having a diameter of I cm. with a length of 5-10 metres.

The question can, of course, be raised whether the viscosity laws, valid for solutions of chain molecules such that the length does not exceed 500Å., still hold for chain molecules with a length of  $1\mu$ . Another difficulty is that the solutions of these substances of high molecular weight show abnormal behaviour; they are not Newtonian solutions, 30 in contradistinction to the solutions of hemicolloids. It was possible, however, to show that the departures from the Hagen-Poiseuille law were due to the length of the dissolved molecules; in the calculation of the molecular weights these departures only manifest themselves in that the resulting molecular weight (i.e., the lengths of the chains) are too low in value and not too high.31 That the extrapolation for the

<sup>&</sup>lt;sup>30</sup> M. Renner, Kolloid. Z., 54, 125, 1931.
<sup>31</sup> H. Staudinger and W. Heuer, "Die hochmolekularen organischen Verbindungen," published by Springer, Berlin, 1932.

calculation of the highest molecular weights is permissible, and that approximately correct values for the size of the molecules of cellulose and rubber result is also shown by the existence of the polymerhomologous series; <sup>32</sup> for the products with the highest molecular weights are connected continuously by means of transitional stages with the hemicolloidal products and with those of low molecular weight. It can be ascertained with such series of polymerhomologous substances that not only does the viscosity of the solution undergo a regular change as the chain increases in length, but that other properties also, for instance the tenaciousness and the elasticity of the solids, change similarly.

Viscosity measurements on the solutions of substances of high molecular weight thus provide the most certain and convenient method of determining the molecular weight of substances for which it is high, it having been shown previously by a chemical investigation that chain molecules are present in the solutions of the substances with the high molecular weight.

### The Sphere of Activity of Long Fibre Molecules.

From the viscosity laws it can be seen that the viscosity of solutions of substances with long chain molecules depends essentially on the number of chain molecules dissolved and on their length. The constitutional peculiarities of the dissolved molecules are, on the other hand, of little importance for the viscosity of their solution. Thus solutions, for instance, of saturated and unsaturated compounds have approximately the same viscosity, e.g., solutions of squalene and perhydrosqualene, <sup>33</sup> and also of caoutchouc and hydrocaoutchouc. <sup>34</sup> The viscosity laws resemble the osmotic laws in many respects. The osmotic pressure of a solution also depends only on the number of particles dissolved and is independent of their constitution. <sup>35</sup>

According to the viscosity laws, equally concentrated solutions of substances, the molecules of which are long chain molecules, contain molecules consisting of chains of the same length whenever the specific viscosities of the solutions are the same. If, for instance, chlorine or bromine is added to an unsaturated compound consisting of chain molecules, solutions of these halogen addition compounds are just as viscous as those of the simple hydrocarbons at the same concentration. Thus the viscosity of squalene in 1.4 per cent. solution is the same as that of perchlor- and perbromsqualene. The molecular weight of these equally long molecules is, of course, not the same, and the number of dissolved molecules of the compounds mentioned is similarly different in a 1.4 per cent. solution. Homopolar compounds with molecules with the same length of chain have therefore the same viscosity in equally concentrated solutions, independent of the weight of the molecules. This can be represented by means of the Einstein formula. According to this, the specific viscosity of a solution is independent of the extent of the sub-division of the disperse phase, and this has been shown to be so in the case of approximately spherical molecules. Here the relationship

$$\eta_{\rm sp.}/c = K$$

<sup>32</sup> H. Staudinger, Z. angew. Chem., 42, 69, 1929.
33 Experiments performed by E. O. Leüpold.

H. Staudinger and R. Nodzu, Helv. chim. acta, 13, 1350, 1930.
 H. Staudinger, Helv. chim. acta, 15, 213, 1932.

holds. In the case of long molecules this formula is valid only with respect to the diameter of the molecules, *i.e.*, solutions containing the same percentages of molecules of different diameters but equal length of chain have the same specific viscosity. Einstein's formula, however, no longer holds if molecules of different lengths are present. In this case the relationship

$$\eta_{\rm sp.}/c = K_m$$
. M or  $\eta_{\rm sp.}/c = K_l$ . L

is valid, where L stands for the length of the molecule. The specific viscosity of a solution having a constant concentration and a constant diameter of the molecules therefore increases proportionally with the chain length.

According to the Einstein law the viscosity of the solution is, moreover, dependent only on the total volume,  $\Phi$ , of the dissolved phase:—

$$\eta_{\rm sp.} = K \cdot \Phi.$$

In the case of molecules having the form of spherical particles, the effective volume of a molecule in solution is equal to the volume proper of the molecule itself. The viscosity of the solution is accordingly independent of the degree of subdivision, it being immaterial whether many small molecules or a few large ones are present in solution. With long, thin molecules, on the other hand, the viscosity increases proportionally with the length of the chain; that volume of a chain molecule which is effective as regards the viscosity is therefore not equal to the volume proper, but increases proportionally with the chain length. This effective volume of a molecule can be expressed for purposes of calculation in terms of a flat cylinder generated by the rotation of the long chain molecule about its axis. We have, therefore,

$$\Phi = \left(\frac{L}{2}\right)^2 \times \pi \times d,$$

where d is the diameter of the chain molecule.

If now the number, n, of the molecules be diminished by, say, one-half on account of sets of two chain molecules each forming single chain molecules of double the diameter, then the total volume of the sphere of activity of these molecules remains unchanged, and the specific viscosity is also the same according to the following calculation:—

Total effective volume, 
$$\Phi$$
, =  $N \times \left(\frac{L}{2}\right)^2 \times \pi \times d = \frac{N}{2} \times \left(\frac{L}{2}\right)^2 \times \pi \times 2d$ .

The experimental fact that, if chlorine be added to an unsaturated long chain molecule, the viscosity of the chlorinated product (i.e., of the thicker molecule) is the same as that of the unchlorinated substance (i.e., of the chain molecule with the smaller diameter) agrees with this. If, on the other hand, the number of chain molecules is halved on account of the formation of long chain molecules of twice the length from sets of two small chain molecules, then the total volume of the sphere of activity of these long molecules is twice as great and the value of the specific viscosity is doubled:—

Total effective volume, 
$$\Phi_{\rm i} = \frac{N}{2} \times \left(\frac{2L}{2}\right)^2 \times \pi \times d = 2N \times \left(\frac{L}{2}\right)^2 \times \pi \times d$$
.

This calculation of the volume of the sphere of activity is not intended to express the view that the chain molecule does actually rotate about

a central axis, for the region of action is rather to be regarded as representing to a certain extent the total effect of the oscillations executed by the chain molecule.

The effective volumes of chain molecules of different size increase proportionally to the square of the length of the chains, *i.e.*, proportionally to the square of the molecular weight. The following (Table III.) shows the increase, as the chain length increases, of the volume proper,  $\nu$ , and of the effective volume,  $\phi$ , of long chain molecules of constant diameter.

Length of the	Volume Proper, v,	Effective Volume	Number of Molecules in r c.c.			
Molecules in Å.	of One Molecule in Å <sup>3</sup> .	of One Molecule in Å <sup>3</sup> .	Calculated using the Volume Proper.	Calculated using the Effective Volume.		
5 50 500 5000	10 <sup>2</sup> 10 <sup>3</sup> 10 <sup>4</sup> 10 <sup>5</sup>	10 <sup>2</sup> 10 <sup>4</sup> 10 <sup>6</sup> 10 <sup>8</sup>	10 <sup>22</sup> 10 <sup>21</sup> 10 <sup>20</sup> 10 <sup>19</sup>	10 <sup>22</sup> 10 <sup>20</sup> 10 <sup>18</sup> 10 <sup>16</sup>		

TABLE III.

Therefore, in the case of a long chain molecule which is 1000 times as long as it is thick, the effective volume is 1000 times as great as the volume proper. If it be assumed that the spheres of activity of the different molecules should not interpenetrate, then a given volume can only contain a thousandth part of the number of molecules it could contain if it were to be filled with only the molecules themselves. If, therefore, a long chain molecule is n times as long as it is broad, the number of chain molecules finding room in a given volume is divided by n, because the effective volume of each molecule is n times greater than the volume proper. With spherical molecules, on the other hand, the effective volume equals the volume proper, and a far greater number of molecules can on that account be introduced into a given volume without one disturbing the other.

### Sol-Solutions, Gel-Solutions and Limiting Concentrations.

A dilute solution, such that the total effective volume of the dissolved molecules is less than the volume of the solution and the molecules, therefore, have freedom of motion, is termed a sol-solution. In such a solution the long chain molecules are in the same normal state of solution as any substance of low molecular weight in a dilute solution.

On account of the large effective volume of long chain molecules, even very dilute solutions of substances of high molecular weight are no longer ordinary solutions, for, as the concentration increases, the total effective volume of the dissolved molecules soon exceeds the available volume. Thus there results a peculiar type of the state of solution, which does not occur with substances of low molecular weight with approximately spherical molecules, as the volume proper and the effective volume are then identical. A solution such that the total effective volume of the long molecules is greater than the volume of the solution is termed a gel-solution. The gel-solutions are connected by a continuous series of intermediate stages with the gels, in which the

mobility of the long molecules is completely repressed. That concentration at which a sol-solution passes into a gel-solution is called the limit-

ing concentration of the substance in question.

The limiting concentrations of solutions of rubbers and balata of different molecular weights are given in the following Table (IV.), the limiting concentrations being given once in terms of the weight of the primary molecule and then, in another column, in percentages.

TABLE IV.

Substance.	Average Molecular Weight.	Aver- age Degree of Polv-	No. of Mols. in 1 c.c. of 0'1 Primary Molar	Effective Volume of One Mol.	Total Effective Volume of all Mols. in 1 c.c. of Primary	Effective Volume as Percent-	Limiting Concentration. Real Solutions Change into Gel-Solutions at Concentrations of	
		merisa- tion.	Molar Solution.	in Å <sup>3</sup> .	Molar Solution.	age of Total Vol- ume.	Prim- ary Molar.	Per- cent- age. Per Cent.
Crude Hevea rubber .	170.000	2500	2.4 . 10 <sup>16</sup>	3.0 108	7.2 1024	720	0.014	0:005
Caoutchouc purified ac-	1,0,000	2,00	24.10	30.10	/ 2.10	120	0 014	0 093
cording to Pummerer; difficultly soluble.	68,000	1000	6.0 . 10 <sub>16</sub>	4·8 . 10 <sup>7</sup>	2.9.1024	290	0.035	0.24
Caoutchouc purified according to Pummerer; easily soluble.	54,000	800	7.5 · 1016	3·I . 10 <sup>7</sup>	2.3.1024	230	0.044	0.30
Balata	50,000		8.0 . 1016					0.31
Masticated rubber .	27,000	400	1.5 . 1017				0.001	0.62
Hemicolloidal polyprenes Degradation product of	6,800	100	6.0 . 10 <sup>17</sup>	4.8.105	2.9 . 1023	29	0.35	2.4
caoutchouc Polyprenes of low mole-	3,400	50	I.2 . 10 <sup>18</sup>	1.2.105	1.4 . 1023	14	0.71	4.8
cular weight	68o	10	6.0 . 10 <sup>18</sup>	4.8.10 <sup>3</sup>	2.9 . 1022	2.9	3.2	24

From this table it can be seen that in the case of caoutchouc degradation products only very dilute solutions are sol-solutions. On the other hand, relatively concentrated solutions of polyprenes of low molecular weight may be produced without coming within the region of the gel-solutions. It follows from the values of the limiting concentration given that most previous viscosity measurements, for instance on rubber solutions, were performed, not in the region of the sol-solutions, but in that of the gel-solutions. Similarly, nearly all osmotic measurements as well as diffusion measurements were not carried out at such a dilution as to correspond to the state of the dissolved molecules in a dilute solution of a substance of low molecular weight. On that account, no simple relationships between the molecular size and the physical properties have resulted from all these investigations of substances of high molecular weight. It is important for the investigation of solutions of substances of high molecular weight to know the respective limiting concentration, so that the experiments may be performed within the region of the sol-solutions.

When a sol-solution passes into a gel-solution, *i.e.*, when the limiting concentration is exceeded, the physical properties do not, of course, undergo a sudden change but a gradual one, for even in a "highly concentrated sol-solution," *i.e.*, in a solution in which the total effective

volume of the dissolved molecules nearly equals the total volume of the solution, disturbances between the long molecules occur, which disturbances gradually become stronger in the region of the gel-solutions. The transition from a sol-solution into a gel-solution is therefore a continuous change. Sol-solutions that are near the limiting concentration and gel-solutions where the limiting concentration has been just exceeded accordingly hardly differ in their properties.

## The Limiting Viscosity.

If the limiting concentration, c, for the solution of a polymerhomologue be calculated, the viscosity of the solution at this limiting concentration can be found from the formula  $\eta_{\rm sp.}=K_m\cdot M\cdot c$ . According to this formula, the molecular weight of different members of a polymerhomologous series is inversely proportional to the concentration of the solution, given that the viscosity is constant. From this it follows that this limiting viscosity is independent of the molecular weight. If, therefore, in a certain polymerhomologous series the viscosity at the limiting concentration of a member of known molecular weight has been determined, then this value of the limiting viscosity is correct for the limiting concentration of solutions of all the other members of this series. Therefore, once a certain limiting viscosity is given, the limiting concentrations of the hemicolloids is far greater than that of the eucolloids.

The limiting viscosity is a highly important quantity for all viscosity measurements on solutions of substances of high molecular weight, for only solutions for which the viscosities are lower than the limiting viscosity are sol-solutions. Only in such solutions may viscosity measurements be performed for the determination of the molecular weight. As it is very easy to determine by means of viscosity measurements whether the viscosity of a solution lies above or below the limiting viscosity, it can easily be decided whether the solution under consideration is of the sol-type or of the gel-type. The limiting viscosities of the different series are given in Table V., and at the same time the limiting

TABLE V.—LIMITING VISCOSITY AND LIMITING CONCENTRATION OF DIFFERENT HIGHLY POLYMERIC SUBSTANCES, CALCULATED FOR A MOLECULAR WEIGHT OF 100,000.

Substance and Solvent.		Limiting Viscosity.	$ \underbrace{ \begin{array}{c} \text{Limiting Concentration.} \\ = \underbrace{ \begin{array}{c} \text{Limiting Viscosity.} \\ \hline K_m . M \end{array} }_{} $		
	nan-etaue	Viscosity.	Primary Mols.	Per Cent.	
Polystyrene in benzene Polyprene in benzene Polyvinylacetate in benzene . Celluloses in Schweizer's reagent Triacetylcelluloses in m-Cresol Trinitrocelluloses in n-butylacetate		0·42 0·71 0·95 1·70 2·50 3·05	0·023 0·024 0·037 0·017 0·023 0·023	0.24 0.16 0.32 0.28 0.66 0.68	

concentrations for highly polymerised products with a molecular weight of 100,000 are entered in order to show at what low concentrations such substances of high molecular weight must be investigated if it is desired to work with sol-solutions.

The high viscosity of solutions containing a relatively small percentage of substances of high molecular weight has, as stated at the beginning, been attracting attention for a long time, and has led to the most varied views as to the nature of colloidal solutions, but, after what has been said, this high viscosity is simply a result of the fact that such solutions are not normal solutions but represent gel-solutions, in which the long chain molecules obstruct one another. To this the properties of the highly viscous solutions of these substances are to be ascribed. fact that the substances of high molecular weight are composed of long chain molecules therefore provides an unstrained explanation of the nature of their colloidal solutions.

#### THE MOLECULAR WEIGHT OF ACETOCELLU-LOSE AND NITROCELLULOSE.

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A method developed in this laboratory by Dr. P. van Campen allows the rapid determination of the osmotic pressure of colloidal solutions.<sup>1</sup> It has been used for measuring the osmotic pressure and determining the molecular (or particle) weight of solutions of acetocellulose and nitrocellulose in different solvents. In the following some of the results will be discussed.

The method rests on a principle already used by Berkeley<sup>2</sup> and Sörensen,<sup>3</sup> namely the partial balancing of the osmotic liquid stream by a hydrostatic pressure exerted on the solution which prevents more or less the entering of solvent into the solution. If the employed pressure exactly equals the osmotic pressure, no movement of liquid in either direction will take place, and if a glass capillary is connected with the compartment containing the solvent, the meniscus will remain at rest. If, however, the applied pressure exceeds the osmotic pressure, the meniscus will be observed to move, since solvent is pressed out of the If, on the contrary, the osmotic pressure is the greater one, the meniscus will move also, but in reversed sense. The velocity of the movement of the meniscus will be proportional to the difference of the applied and the osmotic pressure: extrapolation to zero velocity will, then, furnish the value of the osmotic pressure.

The apparatus will now be very shortly described: it consists of two similar round brass plates, provided with a large number of parallel grooves (0.5 mm. deep), surrounded by a circular groove. On the grooves of both plates two copper gauzes are placed between which the membrane is fixed: an essential point, since in this way changes in shape of the membrane are nearly wholly prevented. The two plates are screwed together, after rubber rings have been placed between them to ensure a perfect tightness. When the diameter of the plates is taken to 15 cm., it is easily seen that a large working surface is obtained, although the volume of the liquid may not exceed 10 c.c. The circular

<sup>1</sup> Van Campen, Rec. Trav. Chim. Pays Bas, 50, 915, 1931. <sup>2</sup> Cf. Findlay, Osmotic pressure.

<sup>3</sup> Sörensen, Z. physiol. Chem., 106, 2, 1919.

grooves in the plates are connected with soldered copper tubes, to the other ends of which glass tubes are attached by rubber tubing. A horizontal graduated glass capillary is connected with the solvent compartment, whilst a tube from the solution compartment leads to a water manometer. Pressure is exerted on this side by means of a bicycle pump.

This apparatus, which was first tried with a hæmoglobin solution in water and a collodion membrane, worked, as one of us showed,<sup>4</sup> equally well with acetocellulose solutions in different organic solvents, e.g. acetone. Of course, collodion could not be used in these experiments: instead, partially denitrated collodion was employed. After a flat collodion membrane had been made in the usual way, it was denitrated by alcoholic ammonium sulphide according to Hess' instructions. It proved to be strictly semi-permeable.

In order to show the usefulness of the method, a few diagrams are given from which the exact linear relation between the velocity of the meniscus movement (abscissæ) and the applied pressure (ordinates) is obvious. It follows that extrapolation is easy, and that the osmotic

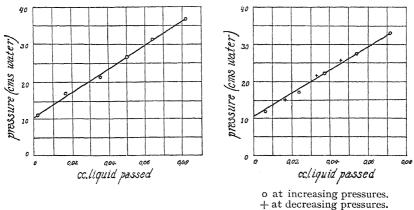


Fig. 1.

pressure is found as the part cut off from the ordinate axis by the straight line drawn through the observed points. The diagrams relate to experiments with a solution of I per cent. technical acetocellulose in acetone.

A slight irregularity in the movement of the meniscus is noticed immediately after a certain pressure is applied, which may be ascribed to a small deformation of the membrane under the influence of the pressure. Measurements were therefore only started five minutes after a new pressure was applied.

Determinations were made at increasing, as well as at decreasing, pressures: the points determined in either way fit equally well on the straight line. Control experiments gave the same results.

The osmotic cell was placed in an electrically heated thermostat, the temperature of which was kept constant within 0.05° C.

The great advantage of this method is to be seen in its rapidity, a measurement being made in one hour instead of needing days, or even weeks. Thereby many control experiments and determinations at different concentrations and at varying temperatures are easily carried

out. Again, rapidity of measurement is particularly important in view of the alterability of many colloidal solutions. Further, one has not to take into account the fact that membranes are often liable to change in course of time and to become more or less permeable; when the membrane remains semi-permeable for, say twenty hours, it is sufficient.

By this method many samples of technical acetocellulose, which had been kindly placed at our disposal by the Cellit works of the I.G. Farbenindustrie at Elberfeld and Leverkusen, have been studied by Dr. Samwel, with the purpose of determining the mean particle weight, and of investigating whether the difference in properties of the samples might be ascribed to a difference in size of the particles.

TABLE I.—Solutions in Acetone,

				t =	o°.	t =	20°.	t =	40°.
	Aceto		Conc.	Osm. Pressure, Cms. Water.	Mol. Wt.	Osm. Pressure, Cms. Water.	Mol. Wt,	Osm. Pressure, Cms. Water.	Mol. Wt.
B2	•	•	1.01 3.07 5.19	6·4 22·6 42·0	36·5 31·5 28·7	8·0 25·2 52·6	31·5 30·3 24·6	7.5 22.8 40.0	35.7 35.8 34.5
В3		•	1.01 3.07 5.19	5·6 21·0 37·0	4 <sup>1</sup> ·7 33·9 32·6	4·6 23·0 46·5	54·5 33·2 27·8	7·4 23·1 40·7	36·2 35·3 33·9
Aı	•	•	1.01 3.07 5.19		_	7·6 25·2 49·2	33.0 30.3 26.3	8·0 23·6 37·5	33·5 34·6 36·8
A2	•	•	1.01 3.07 5.19			10·4 29·0 48·0	24·I 26·3 26·9	7·9 23·4 38·5	33·9 34·9 35·9
А3	•	٠	1.01 3.07 5.19	11·8 26·7 44·2	19·8 26·7 27·2	10·6 22·8 43·7	23·7 33·5 29·6	7.6 23.5 37.4	35·2 34·7 36·9
A4	•		1.01 3.04 5.19		Anadrosia Supervision No arthuris	4·I 20·4 41·I	[60·2] 37·4 31·5	6·9 20·0 35·1	38·8 40·7 39·4
$A_5$	•		1.01 3.07 5.19	ATT TO STATE OF THE STATE OF TH	November Marketon	7·0 20·4 38·9	35·8 37·4 33·2	6-3 19-6 31-0	42.5 41.6 44.6
<b>A</b> 6	•	•	1.01 3.07 5.19	8·5 27·0 39·5	27·5 26·4 33·0	7·6 20·8 42·3	33·0 36·7 30·6	6·1 18·3 32·6	42.9 44.6 42.4
Α7	•	•	1.01 3.07 5.19			3·3 16·4 42·8	[76·0] 46·6 30·2	6.0 17.8 31.6	44.6 45.8 43.7
A8	•	٠	1.01 3.07 5.19	_		6·8 19·5 39·2	36·9 39·2 33·0	5·9 18·2 32·0	45°4 44°7 43°2
<b>A</b> 9	•		1.01 3.07 5.19	5·9 18·8 35·0	39·6 37·9 34·4	5°4 18°1 36°5	46·4 42·2 35·4	6·0 17·6 31·0	44.6 46.4 44.5

Important chemical differences between the samples do not occur: according to the manufacturers, the samples A1 to A9 contain 53 per cent. acetic acid, corresponding with 2·3 acetyl groups in every  $C_6H_{10}O_5$  unit, whilst the samples B2 and B3 contain 55·6 or 55·1 per cent. acetic acid, corresponding with 2·4 acetyl groups. B2 is called low viscous, B3 middle viscous, whereas in the A series the viscosity increases from low (A1) to high (A9) viscous.

TABLE II.—Solutions in Acetophenone.

				t =	o°.	t =	20°.	t =	40°.
	Aceto- cellulose.		Conc.	Osm. Pressure.	Mol. Wt.	Osm. Pressure.	Mol. Wt.	Osm. Pressure.	Mol. Wt.
B2	•	٠	1·01 3·07 5·19	7·1 21·3 —	35·3 35·9	7:5 25:0	35°7 32°6 —	9·2 25·6 45·5	31.0 33.9 32.3.
В3		٠	1·10 3·07 5·19	7·8 22·5 —	32·1 34·0	8·0 25·0	33.2 32.6	8·3 24·5 45·2	34·3 35·4 32·5
Аз	•	٠	1.01 3.07 5.19	_		7·9 23·1	33·9 35·3	8·4 25·2 48·0	33·9· 34·5· 30·6·
<b>A</b> 6	•	•	1.01 3.07 5.19	_		6·8 20·0	39·4 40·8 —	7·4 23·8 42·3	38·5 36·2 34·7
<b>A</b> 9	•	•	1.01 3.07	_		6·7	40·0 42·7	6·8 21·7	41·9 40·0

TABLE III.—Solutions in Benzyl Alcohol.

Aceto-		t =	40°.	t =	= 60°.
cellulose.	Conc.	Osm. Pressure.	Mol. Weight	Osm. Pressure.	Mol. Weight
B2 .	1.01 3.07 5.19	7·8 23·0	34°3 35°5	7·9 24·0 54·0	36·1 36·2 27·2
В3 .	1.01 3.07 5.19	8·0 23·7	33·5 34·4	8·5 24·3 52·0	33°5 35°7 28°3
A3 .	1·01 3·07 5·19	8·0 24·0	33.5 34.0	8·5 25·3 60·1	33·5 34·3 24·5
<b>A</b> 6	1.01 3.07 5.19	7.0 19.8	38·3 41·2	7.5 21.8 54.3	38·0 39·8 27·0
A9 .	1·01 3·07	6·7 19·5	40·0 41·9	7.0 21.3	40.7 40.8

Before making the solutions, the samples were carefully dried in a vacuum exsiccator above sulphuric acid: I, 3 and 5 grams of dried substance were weighed and dissolved in dried acetone in measuring flasks which were afterwards filled up to 100 c.c.

From the measured osmotic pressures the molecular or particle weights were calculated according to the van't Hoff relation, the concentration being taken with regard to 100 c.c. of *solvent*, this having been shown theoretically by van der Waals <sup>5</sup> and by van Laar <sup>6</sup> and experimentally by Morse in his well-known investigation on sugar solutions, to be the only rational way.

Analogous experiments were made with acetophenone and benzyl alcohol as solvent and with a mixture of these liquids in equal volumes. This was done in view of a statement of Wo. Ostwald,? according to which a great many dyestuffs show a maximum degree of dispersity, when dissolved in a mixture of alcohol and water in nearly equal weights.

TABLE IV.—Solutions in a Mixture of Acetophenone and Benzyl Alcohol.

Aceto-		20	o°.	4	o°.	6	0%.
cellulose.	Conc.	Osm. Pressure.	Mol. Wt.	Osm. Pressure.	Mol. Wt.	Osm. Pressure.	Mol. Wt.
B2	1·01 3·07 4·12 5·19	8·o 24·5 —	31.3	7·9 25·0 —	33·9 32·6 —	8·7 25·6 42·5 65·5	32·8 33·9 27·4 22·4
В3	1.01 3.07 4.12 5.19	8·4 24·0	29·9 31·8	7·8 24·6	34·3 33·2 —	8·3 25·2 42·8 62·5	34·3 34·5 27·3 23·5
A <sub>3</sub>	1.01 3.07 4.12 5.19	8·6 26·7 —	29·2 28·6 —	8·3 24·5 —	32·3 33·3	8·7 28·5 47·0 70·1	32·8 30·5 24·8 21·0
A6	1·01 3·07 4·12 5·19	8·0 25·0	31·3 30·6 —	6·8 22·0	39.4 37.1	7·8 25·7 37·5 03·7	36·5 33·8 31·1 23·1
A9	1·01 3·07	Shiphings Mankings	Modulet resid	6·7 20·5	40·0 34·8	7·5 23·3	38∙o 37⁺3

In the following table (V), the results obtained with the I and 3 per cent. solutions in the various solvents are put together.

The conclusion is obvious: the size of the particles of all samples in all solvents is of the same order. The samples B2 and B3 may even be said to have under all circumstances exactly the same particle weight: A6 and A9 show the same when dissolved in acetophenone and benzylalcohol, but deviate when dissolved in acetone and in the mixture of solvents.

<sup>&</sup>lt;sup>5</sup> van der Waals, Lehrb. der Thermodynamik, II.

<sup>6</sup> van Laar, Sechs Vorträge, 29. 7 Ostwald, Koll. Z., 51, 273, 1930.

TABLE V.

Aceto		Acetone.	Acetophenone.		Benzyl Alcohol.		Acetoph Benzyl	Mean.			
	Cellulose.		40°.	40°.	60°.	40°.	60°.	40°.	бо°.		
B <sub>2</sub> B <sub>3</sub> A <sub>3</sub> A <sub>6</sub> A <sub>9</sub>			35·3 35·1 35·6 43·3 45·2	34·2 33·1 34·6 40·1 41·4	32·5 34·9 34·2 37·4 41·0	34·9 34·0 33·8 39·8 41·0	36·2 34·6 33·9 38·9 40·8	33·3 33·8 32·8 38·3 39·9	33.4 34.4 31.7 34.2 37.7	34·3 34·3 33·8 38·9 41·0	

Therefore, it may in general be said that the particle weights of widely different samples of acetocellulose are nearly equal, and that the differences in the behaviour of these substances cannot be ascribed to differences of the particle size.

This is particularly important with regard to the viscosity, as it has been contended by several investigators that a direct and simple relation between the viscosity and the particle weight should exist. Although widely differing viscosities for the various samples had already been mentioned by the manufacturers, Dr. Samwel determined the relative viscosities of I per cent. solutions once again by the ordinary Ostwald method. The results obtained in acetone as solvent at 40° are shown in the following table (VI), in which the specific viscosity, according to Staudinger,

$$\eta_{\rm sp} = \eta_c/\eta_0 - 1$$

is compared with the particle weight:-

TABLE VI.

	ceto- ulose	<u>M</u>	η <sub>sp</sub>	$\frac{M}{\eta_{\rm sp}} \times 10^{-4}$ .	$\frac{M^2}{\eta_{\rm sp}} \times 10^{-8}$ .
A1 A2 A3 A4 A5 A6 A7 A8 A9 B2 B3		 33.5 33.9 35.2 38.8 42.5 42.9 44.6 45.4 44.6 35.7 36.2	1.28 1.50 2.29 2.50 2.61 2.71 2.89 3.23 3.29 2.59 4.01	2·62 2·26 1·54 1·55 1·63 1·58 1·54 1·41 1·36 1·38	8·76 7·66 5·41 6·02 6·92 6·75 6·88 6·35 6·04 4·53 3·21

It is seen that neither a direct proportionality nor a proportionality to the square of the weight is in accordance with the experimental facts.

Analogous results are found with the A-series in the other solvents, the B-samples showing even a greater viscosity for the lower weight. In connection herewith attention is drawn to the fact that, whilst the particle weight does not change at increasing temperatures, the relative viscosity decreases strongly, for instance nearly 20 per cent. between 40° and 60°.

The general conclusion as to a mean particle weight of about 35,000 is in remarkable agreement with the values obtained for cellulose by other investigators. Haworth 8 found 30,000 with a lower possible limit of 25,000, Schmidt 9 at least 16,000, both on chemical evidence. Stamm, 10 using Svedberg's ultra-centrifuge method, calculated 40,000 for cellulose made from linters. It appears, thus, that a cellulose chain is built up from 100 to 200 glucose units. If the number of glucose units in our acetocellulose is calculated from the weight 35,000, we find 130, a little less, therefore, than the values given for cellulose. But this may easily be explained, if it is considered that the cellulose will be very likely partly decomposed on acetylation.

The chemical determinations quoted above point strongly to the view that the particles in the solutions are nothing more than molecules. It would appear that our measurements lead to the same conception. The fact that the particle weight in all solvents is equal is in this respect of great significance, as it is not probable that a substance in colloidal dispersion would have the same particle size in different dispersion

media.

One more ground for this conception is furnished by the result of the spreading experiments, previously carried out by Katz and Samwel, 11 in which it was shown that the thickness of an acetocellulose film on water was only 8.3 A. It is certain, therefore, that at least in one direction the film particles have molecular dimensions and it is difficult to understand why these particles should have a larger size in solution. The only possible explanation would be that the particles have the form of flat disks, the thickness of which would be 8.3 Å, the other dimensions being of colloidal order. All properties, however, of the solutions of cellulose and its derivatives point in the direction of needle-shaped particles and exclude the assumption of the disk form.

A fact discovered by Moll and v. Susich 12 also furnishes evidence in favour of the molecular conception: the X-ray spectrum of acetocellulose, precipitated from its solution, varies with the velocity of its precipitation. This may easily be understood, if the solution is molecular: the spectrum will then depend on the velocity with which the molecules

are aggregated to large crystals which only give sharp lines.

It is therefore considered that the real molecular weights of acetocellulose have been determined osmotically. Of course, there can only be question of mean values, since the substances investigated are undoubtedly mixtures of two or more simple substances, but this can only cause minor deviations, as is shown by a few experiments in which the acetocellulose was submitted to fractional precipitation by water according to Rocha.13 Three fractions were obtained: the osmotic pressure of the middle fraction was determined, and the molecular weight was found to be 37,000, whilst the unpurified substance gave 35,000.

Objections may be raised against the use of the van't Hoff relation for calculating the molecular weight in cases like those considered in this communication. It must be admitted that at lower temperatures the osmotic pressure in the acetone solutions is not exactly proportional

8 Haworth, Nature, 129, 365, 1932.

<sup>&</sup>lt;sup>9</sup> Schmidt, Naturwiss., 19, 367, and 1006, 1931. <sup>10</sup> Stamm, J. Amer. Chem. Soc., 52, 3047, 1930. <sup>11</sup> Katz and Samwel, Liebig Ann., 472, 241, 1929. <sup>12</sup> Mark, Koll. Z., 53, 40, 1930. Meyer and Mark, Hochpolymere Naturstoffe,

<sup>1930,</sup> p. 182.
<sup>13</sup> Rocha, Kollchem. Beih., **30,** 230.

to the concentration, but increases more rapidly, a fact found by all investigators who studied the osmotic phenomena of colloidal solutions. Several empirical formulæ have been tried, without great success. A theoretical formula deduced by van Laar 6 contains van der Waals' constants  $a_1$ ,  $a_2$  and  $a_{12}$ , and cannot be employed, because the values of these constants are unknown.

The reason of this deviation may be looked for in two directions. Firstly, it may be argued that in strong solutions the particles have lost their free mobility, which is essential for the deduction of van't Hoff's law. The observation of a certain amount of structural viscosity in solutions of cellulose derivatives by Nisizawa 14 would give support to this idea, but experiments with the Couette apparatus carried out by Mrs. Büchner de Gruiter with solutions of the same substances as Samwel used, failed to show any such effect.

Secondly, solvatation may be taken into account, which would withdraw a certain part of the solvent. It might be considered that the molecules of solvent, bound chemically or physically to the particle, must no longer be reckoned as the solvent proper, the quantity of which would thereby be diminished. The concentration calculated as grams of substance per litre of solvent would then increase, an effect which would be the more pronounced the greater the concentration.

At 40° the abnormality does not exhibit itself. That higher temperatures will tend to cause a normal behaviour, is on both hypotheses easily understood: it is, however, curious that the transition from abnormal to normal seems to occur so suddenly.

The other solvents do not show deviations from the linear relation, with exception of the 5 per cent. solution in benzyl alcohol and in the mixed solvents. In these cases solvatation therefore would occur in smaller amount or not at all. That, indeed, no appreciable solvatation takes place in acetophenone was shown by the help of the so-called If a certain part of the liquid is taken up by the Gortner effect. colloidal particles, another substance which is dissolved in the colloidal solution will be more concentrated than when it was dissolved in the same quantity of pure solvent. This was proved to be the case for a few examples by Gortner 15 and by Kruyt 16 by determinations of the depression of the freezing point.

The acetophenone solutions lent themselves very well to experiments of this kind, their freezing-point lying at about 20°. Naphthalene was chosen as the substance to be dissolved, and the freezing-points of solutions of naphthalene in pure acetophenone and acetophenone + acetocellulose were compared. The results are found in the following table (VII).

The differences scarcely exceed the experimental errors: if they have real significance, the solvatation will anyhow be very small. It may be calculated that only  $\frac{1}{2}$  per cent. of the solvent is adsorbed by the acetocellulose particles, an amount which would not cause an appreciable error in the value of the osmotic pressure. So, these results are in complete accordance with the normal behaviour of the osmotic pressure observed with this solvent.

In this connection, the experiments with the mixed solvents may still be mentioned. When solvatation occurs, it is not to be expected that

Nisizawa, Koll. Z., 56, 59, 1931.
 Gortner, Coll. Sympos., I, 392.

<sup>16</sup> Kruyt and Winkler, Z. anorg. Chem., 188, 200, 1930.

 $B_3$ 

3.07

Freezing-point Depression. Aceto-Grams. of Grams. of Difference. Conc. Naphthalene. cellulose. Solvent. Obs. Calc. 0.670° o.667° + 0.003°  $B_2$ 1.01 15.024 0.2247 0.735° + 0.007° 0.742°  $B_2$ 14.034 0.2313 3.07 + 0.002° o.697° 15.122 0.2366 0.699°  $B_3$ I.O.I 0.7170 + 0.004° 0.7210

0.2311

14.376

TABLE VII.

both solvents would be adsorbed to the same extent: therefore the composition of the liquid will undergo a change. The liquid passing the semi-permeable membrane will then also have a composition differing from that of the solvent in the other half-cell: during the experiments the composition of this solvent will therefore be varied. view to investigate whether this really occurred, the refraction of the solvent was determined by means of a Zeiss-Abbé refractometer, before and after a number of osmotic measurements. No difference was found even when the liquid had served for three determinations. The conclusion seems to be that in this case also no solvatation takes place.

It is therefore finally considered that the experiments in which proportionality between osmotic pressure and concentration is established,

may very well be used for calculating the molecular weight.

This work is being continued by Mr. Steutel, who is studying nitrocellulose in the same respect. From the results which he will publish in his thesis, it may already be quoted, that the calculation of the molecular weight of this substance is much more difficult than that of acctocellulose, because the osmotic pressure is over no range proportional to the concentration. However, a comparison may be made between equally concentrated solutions of various samples, placed at our disposal by the Deutsche Celluloidfabrik in Eilenburg. With 3 per cent. solutions, molecular weights were then calculated, ranging between 12,000 and 20,000. Although the difference is larger than between the acetocellulose samples, the size of the particles turns out to be of the same order. The relative viscosities, however, vary from 4.11 to 94.6, that is, nearly 23 times, thus showing that a simple relation between particle weight and viscosity does not occur either with nitrocellulose solutions.

#### GENERAL DISCUSSION.

**Professor H. Mark** (Wien) said: There seem to be two fundamental questions: one as to the length and one as to the form of the main valence chains.

In the first case, we have to notice that the different methods, which have been used, have not been applied to the same material and that they all have to be extrapolated in the region of the high molecular compounds.

There is first the chemical method of Haworth and Hirst, which gives us in a very ingenious way the possibility of measuring the chain length of methylated cellulose, if one assumes that the end of every chain is really built up of a free glucose radical and that there is no trace of micromolecular glucose in the sample. Both assumptions seem to be rather reliable. On the other hand, one works with methylated cellulose, so that a certain amount of degradation must be taken into account. The very careful measurements of Haworth and Hirst show, that the degradation cannot be very high, so that the figure of 200-300 may be extrapolated for the native state. The osmotic measurements of Dr. Büchner (and previous investigations of Duclaux and Herzog) are also carried out with slightly degraded products of nitro- and acetylcellulose, so that they also give a lower limit for the chain length of the native state. These measurements are made in a region of 0.4 to 3.5 per cent. Tests have been made as to whether the dependence of the concentration is linear, and it was found that this was so. The conclusion that van't Hoff's law interprets the curve is certainly justified for concentrations below I per cent. But between I per cent. and 4 per cent. one must consider that two influences may cancel each other out and produce a linear function, which does not obey the law of van't Hoff. Several investigators (especially Ostwald, Haller and others) have shown that the swelling pressure tends to raise the curve and to give molecular weights which are below the right value. On the other hand every molecular aggregation would tend to lower the curve and to give higher values for the particle size. One has to be very careful, therefore, in the region of higher concentrations and one should not evaluate the results, even when the curve is linear and seems to fit with the van't Hoff law. But the measurements at low concentrations certainly give reliable values; they lie between 100 and 150 glucose radicals for one chain; one gets, therefore, for the native state again figures in the neighbourhood of 200.

There have to be mentioned two further methods, which give values of the same order of magnitude. Several years ago Herzog applied the X-ray method to determine the average particle size of the micelles in the native cellulose. Sometime later Hengstenberg and Mark carried out improved measurements and concluded that in a very carefully treated sample of native ramie the chains are longer than 120 glucose units. The investigation of artificial silk and other treated samples gave lower values, so that the original value for the native state cannot be very much higher than 200. Finally the diffusion-method led Herzog to a similar value for cellulose acetate and Stamm obtained the same order of magnitude by a very careful centrifugal-investigation of cuprammonium-cellulose.

Although in every case these methods have been applied to different samples one is certainly justified in deriving an *order of magnitude for* the chain length in the native state. The different methods agree as well as may be expected and give values in the neighbourhood of 200 glucose units per chain.

On the other hand, we have all heard that Staudinger has obtained another order of magnitude with the aid of his systematic and extensive viscosity measurements. In the region of micro-molecular compounds there exists a most remarkable agreement between the results of the viscosity methods and any other trustworthy method for the determination of the molecular weight. When we have to face the fact that the viscosity method disagrees with all others in the field of high molecular compounds—i.e., in the case of very long chains—one has to point out that every method must be extrapolated.

I may be allowed to put forward here a possibility, which seems to

me to provide a way out from the above-mentioned discrepancy.

Viscosity measurements are related with the particle in solution. As Professor Staudinger pointed out, all these measurements are carried out in very dilute systems, so that one is entitled to assume that the long chains are isolated and not—or only to a very slight amount—aggregated to higher extents. When these chains are short—between 10 and 100 Å.—the internal friction of the liquid is increased by their presence according to the Staudinger equation.

$$\eta_{\rm sp.}/c = K_m \cdot M \qquad . \qquad . \qquad . \qquad (1)$$

But when they exceed the length of about 100 Å, these chains cannot remain absolutely straight; it seems reasonable to assume, that they are more or less bent and twisted so that they immobilise a certain amount of the liquid and the viscosity rises more than proportionally with the length of the chain. If one adds to the Staudinger-equation a member with the square of the molecular weight 1 multiplied by a small factor  $\alpha$  (about 0.02) we get the following relation

$$\eta_{\rm sp.}/c = K_m M + \alpha M^2 \quad . \qquad . \qquad . \qquad . \qquad (2)$$

When the molecular weight is low, we can neglect the second member and the Staudinger equation proves valid so long as the values of M are not too high. In the region of eucolloidal chains the square member comes into account and leads to smaller values for the molecular weight.

The Staudinger equation purports to describe the viscosity of micromolecular, hemicolloid and eucolloid solutions by one single constant  $K_m$ . That seems to me to be too simple a treatment. In order to describe such a complicated effect as the internal friction of a solution of flexible chains more constants will certainly be needed. The present proposal furnishes a second constant and extrapolates the fundamental Staudinger law in the region of eucolloids. Some years ago it was pointed out by Fikentscher and Mark that one has to take into account a certain amount of solvatation, when the chains get longer and longer, and recently G. V. Schulz has worked with the same idea, so that there is good reason for the belief that eucolloid chains do not obey the Staudinger equation. I would like to point out, that one gets quite a good agreement with the other methods when one applies equation (2) to the measurements of Staudinger himself.

Although it is not yet possible to present anything so definite as a theory, it may be possible to reconcile all the different experimental facts as to the length of the chains in the above-mentioned way. The most probable value for the chain length in native or very slightly treated samples would be between 150 and 300.

There is also a certain disagreement in respect of the shape of these chains. Staudinger concludes from his viscosity measurements, that they are straight and that they make "elastic oscillations like a long thin glass fibre." Our general knowledge as to the behaviour of normal molecules would rather lead to the idea that a long fibre molecule would be more or less bent or wound up, when it is in the gaseous or soluted state. Indeed, a pure statistical consideration shows that a very large molecule has a certain "surface tension" and tries to reach the form

<sup>&</sup>lt;sup>1</sup> This procedure would also be in agreement with the results of a very important work by Werner Kuhn, who has developed a square formula for the viscosity of a suspension of longish particles.

of a sphere. E. Mack has recently measured the Sutherland constant of different hydrocarbons and notices that the cross-section of those molecules cannot be represented by a chain form but leads to a more or less helicoidal shape. R. Wierl observed the same behaviour of α-ωdichlorohydrocarbons by taking electronic-refraction patterns of them. All these facts show that an isolated chain molecule is generally not straight; both the probability and the internal forces between the single members of the chain tend to bend it and the final equilibrium position depends upon the length and nature of the molecule concerned. In concentrated solutions, in the liquid phase, and on surfaces one has to expect another behaviour due to the mutual forces between the different molecules. Here it seems quite reasonable that certain groups or bundles of chains may be formed and that the single chain in such a bundle has a straight shape. It is well known that in condensed surface films one has to assume straight chains, and it seems to be of the utmost interest that Dr. Adam succeeded in detecting a certain flexibility of chain molecules in the expanded state, which corresponds to the gaseous phase.

As in the case of the molecular weight, the viscosity measurements lead also here to results different from those when the other methods have been applied. It seems to be very interesting to get further experimental material on both sides, and there is no doubt that one will

soon get a general and satisfactory view of the whole problem.

Professor H. Staudinger, in reply, said: According to the communication of H. Mark the results about the molecular weight of cellulose obtained by Haworth are in contradiction to my own. This is, however, not the fact, but on the contrary the investigations of Haworth furnish an important proof of my former results on the molecule sizes of celluloses and celluloses-acetates. Some years ago, I had proved, together with H. Freudenberger, that cellulose-acetates due to the different methods of preparation possess average molecular weights ranging from about 10,000 to 50,000. Since it can be assumed that the transformation of cellulose-acetate to methyl-cellulose by Haworth's method of preparation is not connected with a remarkable change of the molecule chain length, these methyl-celluloses having the corresponding molecule sizes of the cellulose-acetates. These are in other words the results arrived at by Haworth.

Preparing cellulose-acetate from cellulose itself, however, there occurs a considerable degradation of the cellulose molecules. Hence, natural cellulose must have a much higher molecular weight than Haworth's cellulose-acetate and methyl-cellulose. Viscosity-measurements by O. Schweitzer and H. Scholz have led to a molecular weight of about 120,000, corresponding to a degree of polymerisation of about 750.

Professor Mark doubts whether it is possible to use the viscosity law, I have found, namely,  $\eta_{\rm sp.}/c = K_m$ . M, for the determination of the molecular weight of cellulose of high molecular weight, and suggests that this is an assumption which still lacks experimental proof. On the contrary, experiments indicate that the viscosity law holds over a very large range, and is not only valid for cellulose-acetates of low molecular weight. R. O. Herzog has recently determined the molecular weights of some cellulose acetates of high molecular weight by means

<sup>&</sup>lt;sup>2</sup> Cf. Berichte d. deutsch. chem. Ges., 63, 2331, 1930.

<sup>&</sup>lt;sup>3</sup> Cf. Berichte d. deutsch. chem. Ges., 63, 3132, 1930; Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose, Verlag Springer, 1932, p. 483.

of osmotic measurements, and also, at the same time, he has determined the viscosity of the solutions. If the  $K_m$ -constant is calculated from these measurements, a value  $10\cdot 2\times 10^{-4}$  results, in agreement with that found by Freudenberger. Now, the cellulose acetates investigated by Herzog possess up to 250 glucose residues in the molecule chain. Hence, the viscosity law is valid for fibre molecules of a length of approximately 20 Å.U. up to 1200 Å.U. On account of this the extrapolation of this law to molecules of a length of 5000-10,000 Å.U. does not appear to be extremely venturesome. It seems, however, probable that this viscosity law is applicable without considerable deviations, to the determination of the highest molecular celluloses.

This viscosity law can only be understood on the assumption that the molecules possess a rigid fibre shape. Naturally the molecules in solution will perform vibrations on account of their freedom of rotation about the carbon bonds, but in the mean position these molecules have a lengthwise extended shape. In order to demonstrate my opinion about these molecules by a comparison, I would compare such a molecule with a thin flexible glass fibre, and not with a wool fibre, which is capable of assuming any shape. Of course, these molecules cannot be compared with absolutely rigid rods. But a rigid shape of the molecules seems to me to be necessary from very general experiences in organic chemistry. The large number of organic compounds is only to be understood if their molecules are rigid.

**Dr. N. K. Adam** (London) said: The molecular models of cellulose indicate the possibility of bending of the chains by rotation about the carbon-oxygen linkages which unite the glucose groups, and my own spreading experiments, as well as those of Katz and Samwel, indicate that some such bending actually occurs under special conditions. Has Professor Staudinger calculated what would be the effect on the viscosity of the solutions of long chain compounds, in which the chains are not straight and rigid but occasionally bend? Haller has shown that the vibrations of long chains may increase the osmotic or swelling pressure of colloids above what would be expected from the simple van't Hoff theory; *i.e.*, the molecular weight calculated from osmotic pressure measurements may be too small if the chains are flexible.

**Professor E. K. Rideal** (Cambridge) said: Evidence against the hypothesis of rigidity of the chains advanced by Professor Staudinger can be obtained from a study of the properties of films of polymers of the type ABAB... where A is a dibasic acid and B a base. These form vaporous films which at very low pressures can form a close-packed network. It is impossible to imagine the formation of such a structure if the chains are rigid. Mr. Hughes will describe similar properties in protein films.

Dr. J. R. Katz (Amsterdam) said: In the case of starch it is possible to compare the molecular weight found by Professor Haworth and Mr. Hirst (3000) with osmometric determinations. M. Samec has done exhaustive work on the osmotic pressures of starch solutions. As a rule he finds much larger numbers, for instance, 100,000 to 200,000; or in the case of soluble starches, 10,000 to 50,000. But in one special case, which is interesting for many reasons, as it seems to be starch in the simplest form, in the least colloidal form, he finds just the number 3000. This starch solution was prepared according to the prescription of Fouard, and called by this author "Solution parfaite d'amidon."

<sup>&</sup>lt;sup>4</sup> E. Fouard, L'état colloïdal de l'amidon et sa constitution physico-chimique, Thèse, Paris, Laval, 1911, p. 50.

Natural starch is extracted carefully with dilute hydrochloric acid (in order to eliminate cations) and then washed with water until the acid is extracted. This starch is now digested under water at 25°-30° (under precautions as to sterility) for three weeks. At the end of this time it has become soluble in boiling water. This solution is filtered through an ultrafilter of collodion. This ultrafiltrate shows only a slight degree of retrogression; this part is filtered off. The solution which remains has, according to Fouard, practically lost its colloidal qualities. Samec, by measurement of the osmotic pressure, found that this solution has the molecular weight of 3000. It might therefore be useful to use starch in this simplest form when determining the molecular weight of starch by other methods.

It is not clear at this time what accounts for the higher molecular weights found from the osmotic pressures in other starch solutions. Do they represent the starch in micellar dispersion? Or is their real molecular weight (the length of the chain) accordingly larger? It will be necessary to clear up this point before we can depend on the numbers found for the molecular weights of starch.

Dr. J. R. Katz further said: There are several reasons for believing that long chain molecules may often have the form of long somewhat rigid straight rods. Of course, a certain percentage of the molecules must lie in very complicated forms, which change all the time; for example, it is a well-known fact in organic chemistry that oxyacids have the strongest tendency to form lactones when the two active groups are in the 1.5 or in the 1.6 position. But the X-ray diagrams of liquids, made approximately at the same time in 1927 by Professor Stewart (in Iowa City), by the collaborators of Professor Raman in Calcutta and by myself together with J. Selman (in Amsterdam), seem to point clearly in a very different direction.

The X-ray spectrum of the normal aliphatic alcohols contains chiefly two interferences, the one having almost the same diameter whatever be the number of carbon atoms, while the other one shows the existence of a period of identity (calculated from Bragg's formula) which increases by the same amount per carbon atom. The existence of this second interference-circle has been doubted in the case of normal fatty acids which it is difficult to prepare in a very pure condition. Its existence is beyond any doubt in the case of the normal alcohols.

We must conclude that a large part of the molecules of such liquids lies in small groups, as in a somewhat irregular crystal lattice, that their form must be somewhat rigid, and that they have the form of a straight rod. Only a small part will have the irregular forms mentioned above.

Some experiments of Professor Ingold on the dissociation constants of dibasic acids seem to show that in solution, too, such molecules might have the form of somewhat rigid straight rods.

Mr. S. M. Neale (Manchester) pointed out that in the work of Professor Staudinger it was inferred that the nature of the solvent was of little importance. This could hardly be maintained, however, in the case of cuprammonium solutions of cellulose, where the specific viscosity was almost inversely proportional to the concentration of copper.

The viscosity of a solution in cuprammonium is in general use a highly sensitive index of the slightest degradation in the structure of

<sup>&</sup>lt;sup>5</sup> See my two articles, Z. angew. Chemie, 41, 331, 1928; Réunion Internationale de Chimie Physique, Paris, 1928, p. 398; where the literature on the subject is mentioned.

cellulose, and it was therefore important, in the use of viscosity as a criterion of molecular size, to define exactly the condition of the cellulose used. Thus in 0-5 per cent. solution carefully bleached cotton was thirty times as viscous as rayon. In a solution of 0-005 fundamentally molar this corresponded to a specific viscosity ratio, and therefore a ratio of molecular weights, of roughly 12 to 1. Smaller but quite important variations occurred within the range of the technical bleaching of cotton. The conversion of viscosities in cuprammonium from one concentration to another could be accurately made by the empirical equation of Farrow and Neale 6 which held good over a viscosity range of several thousand fold. Whilst plausible theoretical reasons could no doubt be advanced, it was perhaps unfortunate that in Professor Staudinger's theory it was necessary to assume a relation between viscosity and concentration which actually held good only over a relatively minute range.

In connection with the straightness or otherwise of long molecular chains in solution, it seemed probable that in a viscosity measurement the shearing of the liquid will tend towards a straightening of the chains. Increasing straightening with increasing rate of shear might account for the anomalous behaviour of high polymer solutions, in that the apparent viscosity decreased as the rate of shear increased. Such an explanation would be in accord with the fact that this anomaly was more evident in more concentrated solutions, where the mutual interference of the long molecules would be more pronounced.

In speculation on the viscosity of these complex solutions, however, we should not lose sight of the fact that the mechanism of viscosity even in simple liquid mixtures was not well understood.

**Dr. T. Malkin** (Bristol) said: The tetrahedral zigzag chain which exists in crystals of long chain compounds and to some extent in long chain liquids is a symmetrical structure. It appears to me, that in the absence of any strong directing force, this arrangement is the most statistically probable whether the long chain compound is in the state of solid, liquid, or homogeneous solution. That is to say, there seems to be no obvious reason why the forces on one side of the zigzag should be in any way different from those on any other side, as they would be, for instance, in an irregular zigzag.

It is admitted that the chain can assume other forms, as it must do in ring compounds, but in the formation of these (e.g., from the dibasic acids) strong directive forces tend to draw the end carboxyl groups together, nevertheless, it is well known that if such dibasic acids have more than 5, 6, or 7 carbon atoms, the yield of ring compound is exceedingly low. It therefore appears that as the number of intermediate carbons increases, the attraction of the end groups is resisted, suggesting that the chain straightens out to the usual zigzag form.

I think it is worth noting, in connection with helix formation, that left- and right-handed optically active forms should theoretically be possible and that so far such optical isomers have never been observed.

**Dr. Adam** (London) said: Dr. Malkin's suggestion that the most stable position of an isolated chain is the flat zigzag involves the assumption that this configuration of the molecule has the least potential energy of all possible configurations. In the case of a single isolated molecule I do not think this can be the case, since there are attractive forces all

round the chain, which would be partially satisfied if the molecule were to coil up into a compact form such as a helix. The mutual attractions between different parts of the "surface" of the long molecule would provide the force necessary to coil the molecule. I agree that these forces would be symmetrical—i.e., that the tendencies to bend the molecule to one side or to the other would be equal; but surely this is not a reason for expecting that the molecules would not bend or coil? On the contrary, the symmetry of these attractive forces would have the result that the numbers of molecules in right- and left-handed helices would be equal. This accounts for the absence of optical antimers: to use the language of stereochemistry, the symmetry of the coiling forces would not provide suitable conditions for an "asymmetric synthesis" of either right- or left-handed helices. Also, if one or the other form of helix were to predominate temporarily, I think that the thermal motions would rapidly cause "racemisation," i.e., uncoiling and recoiling until the numbers of molecules in opposite configurations were equal.

These remarks, however, apply only to molecules in free space. In dilute solution, under the conditions of osmotic pressure or viscosity measurements, it seems to me quite likely that the majority of the molecules are straight and possibly the corrections to Staudinger's viscosity equation due to bending of the molecules are small. The possibility of the existence of such corrections ought, however, to be taken into account.

Mr. C. Diamond (*Coventry*) said: It appears to me that we are asked to consider the merits of the two methods used for determining the length of the cellulose chain, the viscosity method of Staudinger and the hydrolysis of the methylated cellulose carried out by Haworth.

Of these two methods, I am very much inclined to support the viscosity method, for the solution of a cellulose in Schweitzer's solution can be carried out, if precautions are taken, without any appreciable effect on the cellulose, whereas considerable experience with the process of alkylation of cellulose, leads me to believe that appreciable depolymerisation must occur during the preparation of cellulose ethers. Even if the alkylation did not produce any appreciably depolymerisation, yet it is certain that the degradation would be very heavy during the acetylation stage, in those cases where Haworth has employed an acetate for the preparation of his ethers.

The depolymerisation of the cellulose ethers receives support from the observation that when spun into threads they are amongst the weakest in strength so far obtained from cellulose and its derivatives.

Dr. Adam's theory of the low lateral adhesion of the cellulose ethers does not seem to be the explanation since this low strength per unit of cross-sectional area is obtained to about the same extent with both coarse and fine filament yarns.

Any formula for the cellulose molecule should take into account the facts that in the acetolysis of cellulose, only 33 per cent. of the cellulose has been converted into cellulose, the remainder being converted into glucose and furthermore some explanation is required to account for the inability to acetylate cellulose after it has been mercerised with caustic soda, particularly since the mercerisation process also appears to affect the X-ray spectrum.

**Dr. Hans Machemer** (*Dresden and Birmingham*) said: The method of arriving at the molecular weights of methylated cellodextrin chains

is based on estimation of the tetramethyl glucose, derived from the non-reducing end-group. These results I have confirmed not only by means of viscosity measurements, in Staudinger's laboratory, but also by another chemical reaction involving the reducing end-group of the cellodextrin chain.

By means of iodine oxidation, the aldehyde groups are fully oxidised within twenty minutes, whereas an hour's further treatment under the same conditions only carries the absorption of iodine 10-15 per cent. further. Changes in the  $p_{\rm H}$  of the solutions have exactly the same effect as in the case of cellobiose. The iodine number determination, which I have similarly checked with viscosity readings, agree well with the above. The reducing end-group of the cellodextrins gives, by methylation, a glucosidic group, which can be tested for and estimated roughly by a hydrolysis method, similar to that applied by K. Freudenberg to methylated cellobiose and cellotriose.

Comparative results for typical fractions are appended:—

	Ace	tates.	Methylated Compounds.				
Method After.	Bergmann- Machemer.	Staudinger.7	Haworth- Machemer.	Staudinger <sup>8</sup>	Freudenberg- Soff. <sup>2</sup>		
Number of hexose units	20 14 11	21-18 14-13 11- 9	26 23 13	28-22 21-15 13-11	~ 30 (approx.) ~ 20 (approx.)		

It must be emphasised that these are merely average values for chain length, perfect fractionation of the higher molecular cellodextrins being impossible. Since these results for methylated and acetylated dextrins agree *inter alia*, it seems that no degradation can occur in methylation. Cellodextrin acetates of 10-20 glucose units give 80-90 per cent. of methylated product, which fractionates to a chain length of 10-25. All cellobioses, trioses and tetraoses are eliminated before methylation by treatment with 2N-sodium hydroxide, the cellodextrins after methylation are completely insoluble in hot water: indeed, the mother liquors from methylation yield no dextrin whatever of smaller chain length than 10.

The number of glucose residues in the cellodextrins has thus been found, by several mutually agreeing methods, for chains containing up to 20-25 units. Comparison of the viscosities of these materials  $(\eta_{\rm SP}/c=2\cdot5\cdot7)$  with the very much higher viscosity of cellulose  $(\eta_{\rm SP}/c=>30)$  inclines us to the opinion that this last must have a very large molecule. Chemical methods actually indicate a minimum length of 100 hexose units. The extension of the iodine number method to cellulose is unlikely to give any but rough results, for the end-groups form such a small proportion of the whole that it will be difficult to disentangle their reducing action from that of the rest of the molecule.

**Professor Staudinger** (Freiburg i. Br.) said: H. Machemer has investigated the different cellulose acetates of Haworth by viscosity measurements. In this case also, the  $K_m$ -constant is of the same order of magnitude, though the molecular weights were obtained by quite a different method, namely by the determination of a characteristic

8 Cannot be applied to higher cellodextrins.

<sup>&</sup>lt;sup>7</sup> Extreme conditions 20-60° in Dioxan and m-Cresol.

end-group. The utility of the end-group method for the determination of molecular weights has been proved to be free from objection in the case of products with a definite constitution, such as the polyoxymethylene diacetates and the polyoxymethylene dimethyl ethers. For these very simple products (as well as for the polyethylene oxides) the molecular weights (i.e., the chain lengths) were determined by three different methods:—

by the cryoscopic method;

2. by the determination of the end-groups;

3. by viscosimetric measurements.

For all these products the three different methods of measurement furnished results in good agreement so that the utility of the viscosimetric method for the determination of chain lengths can no longer be doubted.

Mr. S. M. Neale (Manchester) suggested (in regard to the paper of Haworth and Hirst) that the character of the cellulose used should be defined by the exact empirical tests now available. It might be found that the "molecular weight" was not a constant, but was entirely dependent on the pre-treatment of the sample of cellulose used. It was unsafe to argue from experiments with cellodextrins that the method caused no serious breakdown of cellulose itself since a proportion of breakdown—say one out of every two hundred linkages—negligible in the former case might have a large effect on the average chain length in the latter.

Mr. W. Harrison (Kilmacolm, Scotland) (communicated): The work of Haworth and Hirst indicates that in cellulose tenters one glucose residue in every 100-200 behaves differently from the remainder. It does not prove that the cellulose molecule consists of 100-200 glucose units nor does it prove that the cellulose molecule is 100-200 glucose units in length; it may be a result of an irregular distribution of glucose units attached as side-chains.

The valuable work of Staudinger definitely indicates that the viscosity increases with the length of the molecule in solution. Since, however, Einstein's law shows the viscosity to be proportional to the total effective volume, Staudinger's work does not tell anything about the width of the molecule or the number of chains attached sideways in the molecule, hence gives no indication of the molecular weight of cellulose in solution.

Since it is agreed that the osmotic laws apply to rigid molecules up to macroscopic dimensions the very interesting work of Büchner apparently indicates that the molecular weight of cellulose acetate is around 35,000 or equal to 122 glucose units. The remarkable fact, however, is that the molecular weight varies very slightly among eleven different samples, of viscosities ranging from 1 to 4 in relative units. To bring Staudinger's work into line with this, one would need to assume an adjustment between length and breadth of the molecule to give constant weight, a rather wide assumption.

I am, however, of the opinion that the osmotic laws will not apply

to long flexible molecules.

It is inconceivable that a molecule composed of two rigid spheres attached by a long flexible chain—similar to two cannon-balls attached by a chain—would behave the same as a rigid molecule of the same total weight. At the least it would behave as two separate molecules of weight equal to the two separate rigid spheres. If this is the case the mean kinetic energy of a very long flexible molecule may increase with the length of the molecule. Osmotic measurements would then indicate

molecular weights up to a certain maximum and no higher for the same material of increasing length of chain. Chain structures of greater weight per unit length would, of course, give osmotic pressures indicating higher molecular weights again up to a maximum.

An opinion expressed by the writer many years ago is that the length of the cellulose molecule as present in cotton fibres is equal to the length of the fibre, the molecule is continuous but not necessarily straight or regular. Up to now there is no evidence in disproof of this opinion, so far no one has succeeded in re-polymerising cellulose after it has been degraded or depolymerised even to the slightest degree. Even though during chemical treatment the fibre remains intact one cannot reverse the process and get back fibres in their original condition.

- Mr. C. Diamond (Coventry) (communicated): Dr. Hirst in the discussion has stated that the figure of the number of glucose units is a minimum one, but Haworth at the British Association Meeting at York was very insistent that their figure was close to the maximum. It should be possible to arrive at some conclusion as to the degradation during his methylation if two celluloses, differing appreciably in their degree of degradation, were put through his methylation and hydrolysis operations and the percentage of tetramethyl glucose determined in each case.
- Mr. G. F. Davidson (Manchester) said: I think previous speakers are probably wrong in concentrating on the methylation process as a possible source of degradation, and that degradation is more likely to occur during the acetylation. The molecular weight found was compared with that obtained by the Bergmann-Machemer iodine method, both in the work on the cello-dextrins and on cellulose acetate, and this seems to me an unsound procedure. The use of the Bergmann-Machemer method depends on the assumption that each chain-molecule has a reducing group on the end of it, and this assumption is almost certainly false. It is well known that the reducing power of chemically modified celluloses is almost completely destroyed by treatment with hot dilute alkali, and since the celluloses used by the chemist have all been subjected to such a treatment during their purification, it follows that few of the chain-molecules in the celluloses used as starting materials for the preparation of cellulose acetate or cello-dextrins will have a reducing group on the end of them. This must introduce an error into the determination of the molecular weight by the Bergmann-Machemer method which will be the more serious the less degraded the cellulose or cellulose derivative investigated.
- **Dr. F. T. Peirce** (communicated): To the technologist, the unit of cotton is the hair. Scientific technology is based on the study of the behaviour of textiles in terms of that of the single fibre—as a whole. If it penetrates farther, it is only to explain the differences and changes in hairs. Progress in colloid chemistry has brought that finer analysis into the sphere of technical interest and into relation with the great amount of investigation on the hair as a unit.

To the colloid chemist, cell structure has been an unwanted complication in the study of cellulose in terms of molecular units. Having now established the main features of the molecular order, the focus of interest is, however, shifting to the aggregation of the cellulose chains. That aggregation produces the cotton hair, is conditioned by the structure of the hair and must be studied as an aspect of the growth of that unit.

<sup>&</sup>lt;sup>9</sup> Cf. Haworth and Machemer, J. Chem. Soc., 2270, 1932.

Study of the hair as such will often suggest the right choice between alternative hypotheses which equally explain colloid data.

Microscopy, in the first place, shows the cotton hair to have a structure built up of fine spiral elements, which reverse at irregular intervals. This complex pattern of reversing spirals is continuous from primary wall to lumen, through fine and regular concentric shells of daily growth. This is not the result of precipitation of small crystals from solution, which could not be so independent of gravitation, geometry and the local and temporary changes of form in a hair struggling for space among a tangled mass. The nucleus, on which all crystalline growth depends, is the pre-existent cellulose surface, at the interface with the protoplasmic solution. But that surface has the cell wall pattern as well as the crystalline order and the deposition must conform to both.

The powerful and unique cohesive bonds which hold small molecules in perfect crystals cannot compromise with local distortions. The perfect order is adopted, or none, and gross structures are formed by aggregations of small crystals or by the growth of large crystals by molecular solution and redeposition. Such rigid crystalline order cannot be presumed in cellulose, where the conditions are essentially different. On the unique nucleus of the interface, cellulose is deposited in long chains, flexure of which demands energy of only the same order as the elastic strain of intermolecular fields. Being fully hydrated, the lateral cohesion has little rigidity and a continuous structure can grow into the pattern of the wall by a compromise between the force fields of valency, crystalline structure and elastic strain. On dehydration, the bundle of continuous chains collapses into crystalline order, where and as far as the pattern allows. Can it be shown that such an array of atoms would diffract X-rays otherwise than as observed or as an assembly of discrete perfect crystals.

Returning to microscopy, markings may be developed at right angles to the structural spirals by swelling hairs after chemical attack. Such markings are readily explicable as cleavage lines following a crystallographic plane. Till recently, this would have been a wild speculation; the more obvious and safe explanation being to regard these three normal sets of markings—quick spiral, slow spiral and growth rings—as defining a brick-like structure. Micelles were demanded for lack of grounds for postulating crystalline structure and their hypothetical necessity vanishes with the advent of the latter. Why should discrete micelles part along a line of weakness of a known crystalline structure, developed by attack of the valency forces therein?

Degradation greatly facilitates the solution of the cellulose in swelling agents. It is even doubtful whether truly raw cotton can be completely dissolved. The viscosity of the solutions exhibits ageing phenomena and varies with the solvent in ways which show that the coherence is only of the order of the forces of osmosis or swelling and that the aggregates are changeable; not crystallites released as such from the hair wall. Esters, to which the same crystallite theory is extended, may even be spread into single layers of hexose chains.

The colloid aspect of the problem of the structure of cotton is the aggregation of indefinitely long hexose chains into the pattern of the cell wall. There are crystalline and amorphous features. Are there bounded and separate regions of crystalline and amorphous structure or do the chains individually and locally fit into perfect or imperfect order according to the exigencies of the pattern? The latter alternative

tive gives a much more general and consistent account of the mechanical behaviour of the hair, and its relations with moisture.

The question reduces mainly to that of the types of cohesion within the structure. These are of three fairly distinct types—the primary valency bond of the chains lengthwise, the lateral cohesion of the crystalline structure and the lateral cohesion where the crystalline order is interrupted. The first is very powerful and unaffected by moisture, the last weak and sensitive to moisture. One or other must supply the resistance to tensile rupture.

In both degraded and regenerated cellulose, where the chains have been comminuted, tensile strength plainly depends on the last. It is low and diminishes with moisture absorption. In raw cotton, the tensile strength is remarkably high and is increased by moisture. Before comparing the breaking load with any expectation from the rupture of molecular chains, it is necessary to enquire what number of such chains will be contributing their full breaking load to the longitudinal component of tension at the instant of maximum load. A variable and often large percentage of hairs break at gross abnormalities, which may be detected by low power microscopy. In a test on 192 hairs, 72 predicted breaks at abnormalities gave a mean breaking load of 2.6 grams, the remaining 130 gave 5·1 grams. Even these latter breaks represent not an average but the weakest points in centimetre lengths. On a similar sample of hairs, a mean of 4.2 grams was obtained on centimetre lengths, 7.8 grams on millimetre lengths. 10 Looking still more closely, it was found that breaks did not even then occur in regularly convoluting portions but at those contorted portions of the pattern where the spiral reversed its direction twice in a very short interval. On millimetre lengths of fine, regular hairs, a breaking length of 58 kilometres has been observed, but the actual strength of the regularly convoluting structure must be considerably greater. Nor is the breaking load of a bundle of parallel elements equal to the total breaking loads of these elements. Only the rupture of the molecular chains could explain this strength and its resistance to moisture. The increase in strength over the low range of humidity is explicable by the lubrication of the lateral cohesion which allows better stress distribution and the release of tangles which might cause rupture at an earlier portion of the extension. Such releases are indicated by discontinuous jumps of extension in wet hairs slowly extending under moderate load.11

Whereas materials, such as viscose, which resist extension by internal viscosity show an extension load ratio which increases with load, that given by cotton hairs decreases. Moreover, the low ultimate value of this ratio is not appreciably affected by humidity and is equal to the slope given by the immediate recovery from load. The earlier, easy extension varies with humidity—with the initial swelling or separation of the spirals which determines the amount of structural extension possible. The portion ascribable to the elastic extension of the dry crystalline lattice is not more than 4 per cent., and there is no sign of the viscous flow which must precede rupture when this occurs by the relative tangential movement of micelles. The phenomena of elastic imperfection, though the evidence is too complex and indirect for review here, also indicate the absence of flow but only that semi-permanent local strain redistribution of a permanent pattern that may be called, after Weichert, "epibolicity."

Brown, Mann and Peirce, Shirley Institute Memoirs, 9, 1, 1930; or J. Text.
 Inst., 21, T186, 1930.
 Collins, S.I.M., 3, 271, 1924; or J.T.I., 15, T519, 1924.

In the absorption of water, the shape of the isotherm, its variation with temperature, the rate of absorption, heat of absorption, specific volume and effect on rigidity all demand the recognition of an intense. in fact stoichiometric, absorption of the first molecules on a dry surface followed by a weakly bound layer. Well before saturation, there are more than two water molecules to each hexose group. Though the accessibility of the latter may vary more or less and a greater concentration than this be possible locally, the lowest estimate of the size of micelles from which water is supposed to be excluded would demand an unreasonable range of action of the surface attraction; and an excessive separation of the infrequent absorbing surfaces would be demanded to explain the swelling. A theory attempting the quantitative explanation of these phenomena has been developed on the postulate that every hexose group is more or less accessible.12 Though this necessarily involves a large element of speculation, a more qualitative consideration of the evidence does seem to demand that postulate. A whole field of research cannot be condensed into a short note and the original accounts are involved with much matter of more technical interest. A general reference to a list of papers 13 may assist colloid chemists to discover evidence hidden in textile technology.

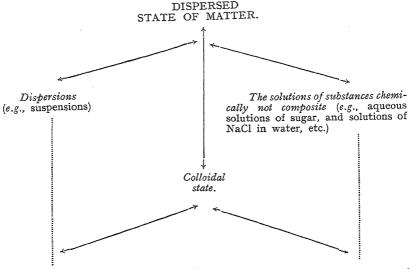
X-ray evidence has been used to indicate that the absorbed water in cotton is inter-micellar. This term becomes rather vague in meaning on the above view, and an effective critique of the evidence would have to begin from the immediate data of the diffraction photographs. Permutoid swelling, to use the clear terminology suggested by Katz, is to be expected only where the foreign molecule enters in stoichiometric relation and that alone. Its occurrence with sodium hydroxide shows that the interior of the crystalline regions is accessible under forces which may be greater but not of different order from those exerted by the initial absorption of water. The added general absorption of water which accompanies the more energetic beginnings would prevent the formation of a new crystalline order and the absence of appreciable change of pattern may mean no more than that; first, the absorption goes preferentially to regions already disorganised; secondly the crystalline regions penetrated cease to diffract so long as the water molecules are present. Admittedly, however, there is no clear alternative picture of the cellulose-water system which so evidently satisfies the X-ray data taken alone as the view that the water is excluded from the crystalline lattice. But it is not certain that less obvious alternatives, suggested by the structure and behaviour of the cell as a whole, have been fully explored, as all the data have been interpreted without question on the analysis of the diffraction of uncompromisingly perfect crystals.

Professor P. P. von Weimarn (Kobe, Japan) (communicated): In the excellent paper of Professor H. Staudinger, as well as in his earlier numerous publications, mention is made, among other questions, of the important question of the position occupied by solutions of highly-molecular substances among other representatives of the dispersed state of matter.

Perhaps my views on this subject would be not altogether without interest. In order to express them as briefly as possible I shall confine myself to a quotation from one of my papers previously published (Japanese Journal of Chemistry, 3, 71-73, 1928):—

<sup>Peirce, S.I.M., 8, 69, 1929; or J.T.I., 20, T133, 1929.
Peirce, J. Text. Inst., 23, P16, 1932.</sup> 

"By the following scheme 14 may be expressed the subdivision of the colloidal state of matter into two main species: dispersoidal and solutoidal.15



Dispersoidal state (dispersoidal solutions of sulphur in water, NaCl in benzene, etc.).

Solutoidal state (e.g., solutions of caoutchouc in benzene, aqueous solutions of certain salts of fatty acids, of certain soaps, etc.).

"Dispersoidal solutions of solid substances in liquids are extreme cases of suspensions; or in other words, they are suspensions of extremely small crystals (ultra-microcrystals) and of their aggregates.

"Solutoidal solutions are extreme cases of true solutions; or in other words they are true solutions of chemically composite (high-molecular) substances, i.e., solutions containing extremely large molecules and associations of molecules.

"The dispersoidal state, using the effective expression of McBain, 16 is a state thermodynamically unstable, while the solutoidal state is a state thermodynamically stable, 17 for it is a state of true solutions of chemically composite (high-molecular) substances, as stated above.

14 This scheme does not differ in essentials from those given in my previous papers on Wolfgang Ostwalds' classification. Compare Koll.-Zeitschr., 3, 27, 1908; 7, 155, 1910. Revue générale des Colloides, 4, 130, 1926. Cf. also Koll.-

Zeitschr., 49, 134, 1927.

15 The term "Solutoide" was suggested by me in 1910 (Koll. Zeitschr., 7, 155).

16 James W. McBain Koll.-Zeitschr., 40, 1, 1926.

17 It should be noted that the solutoidal state is thermodynamically stable only when exhibited in solutions, and not in precipitates (gelatinous precipitates, jellies). All the forms of the precipitates of the solutoidal solutions are thermodynamically unstable, not excepting the most typical jellies. Just in the same sense they are thermodynamically unstable as, for instance, a precipitate of NaCl crystals is unstable when it is in contact with its aqueous mother liquor, under constant temperature and pressure. This precipitate undergoes changes up to the time when the largest and the most homogeneous of crystals swallows up all the others; and only when this single and most homogeneous crystal remains alone in the mother liquor, the thermodynamical equilibrium will ensue. Solutoidal jellies also undergo with time, continual changes; but sometimes so protractedly as to create an illusion of an equilibrium already existing; but neither these jellies nor glasses represent systems thermodynamically stable; here we have, in extreme cases, examples of the so-called false equilibrium.

"But also, of course, chemically composite (high-molecular) substances may be obtained in a dispersoidal state in dispersion media, in which they have enough slight solubility (practically insoluble); for instance, gelatin in alcohol, caoutchouc in aceton, cellulose in water, etc., at room temperature.18

"Also the transition from the state of solutoidal solution of these composite substances into the state of dispersoidal solution is often accomplished with extreme ease, by lowering their solubilities through

lower temperature.19

"The dispersoidal state is a universally possible state of matter for chemi-

cally simple substances as well as for chemically composite ones.20

"The solutoidal state is the state appropriate to chemically composite substances, as stated above. Consequently, chemically simple substances can be in a solutoidal state only under the form of their gigantic solvates. i.e., the solutoidal state is a universal one in so far as the gigantic solvation of any substance can be reached.

"And such a solvation is in principle attainable under right condi-

tions 21 for any substance.

"Thus chemically simple substances cannot be obtained in a solutoidal state without complicating them by gigantic solvation and by association.

"Although, as stated above, dispersoidal and solutoidal states differ from each other in the same sense as thermodynamically unstable systems differ from those thermodynamically stable, it proves to be no easy task to discern between the extremely stable dispersoidal solutions and solutoidal solutions.

"By introducing the 'dispergators' in dispersion media which practically do not dissolve the substance dispergated therein, the degree of stability of dispersoidal solutions of chemically simple as well as of chemically composite (high-molecular) substances, may be raised so as to render exceedingly difficult, if not altogether impossible, the decision of the problem for certain cases at the present time, whether these disperse systems belong to the one or to the other, of the main species of colloidal state. The last mentioned appertains particularly to the dispersoidal solutions of chemically composite substances dispergated by means of powerful dispergators."

Professor H. Staudinger (in reply) wrote: Different propositions exist as to the classification of colloids. Freundlich and other investigators distinguish between lyophilic and lyophobic colloids. Wo. Ostwald subdivides colloidal systems into suspensoids and emulsoids. In the latter case he assumes a colloidal distribution of a liquid phase in a liquid dispersion agent, and puts into this group the solutions of rubber and other high molecular substances. Prof. v. Weimarn distinguishes

between dispersoidal and solutoidal solutions.

In all these classifications the internal structure of the colloid particles is not sufficiently taken into account. Thus, colloids of quite different structure and behaviour are associated in one group. To the solutoidal solutions of Professor v. Weimarn belong, e.g., solutions of rubber in

19 In these cases the solubility drops promptly when lowering the temperature within the limits of some tens of degrees.

<sup>20</sup> P. P. von Weimarn, Journ. of the Russ. Chem. Soc., 28, 263, 1906, etc. Cf. my paper in "Colloid Chemistry, Theoretical and Applied," ed. by J. Alexander, Vol. I., pp. 27-102. The Chemical Catalog Co., New York. 1926.

<sup>21</sup> P. P. von Weimarn, l.c. Footnote 7.

<sup>18</sup> Compare my paper in Revue générale des Colloïdes, 4, 132, 1926. Cf. also 7, 153, 1929.

benzene and solutions of soaps in water, though the colloid particles of these two substances have quite a different structure. The colloid particles in solutions of rubber in benzene (as well as those of cellulose in cuprammonium hydroxide) are the molecules themselves. In this case long fibre molecules are present, possessing colloidal dimensions only in one direction, i.e., their length. It has recently been possible to elucidate the structure of these molecules by organic-chemical investigations. Hence, in the case of rubber and cellulose we have high molecular substances built up of giant molecules or macromolecules. These high molecular substances are connected by continuous transitions with the low molecular substances of the same structure. Thus, there exist polymer-homologous series, e.g., of polyprenes, the first member of the series being isoprene and the end member being rubber. In the polymerhomologous series of cellulose the first member of the series is represented by cellulose, which by transition members is connected with the highest molecular cellulose. In the colloidal solutions of soaps, however, micelles are present which arise through the association of numerous relatively small molecules. Such a micellar structure was formerly attributed to the high molecular substances by most of the investigators, but must be considered incorrect on account of the chemical investigations.

Therefore a new classification for colloidal systems is necessary, the different groups being as follows:—22

I. Suspensoids and Emulsoids.—Any solid or liquid substance may be colloidally distributed in a suitable dispersion agent. These colloid particles generally possess a spherical shape; hence, these colloidal systems show low viscosities, because high viscosity occurs only if long extended molecules are present in solution.

II. Molecule-Colloids.—In this group the colloid particles are the molecules themselves. Marcomolecules of a molecular weight of 100,000 and higher may occur in this case. Thus, in these molecules 10,000 and more atoms are bound by primary valence. Most of these molecules have fibre shape. Therefore their solutions show a particularly high viscosity, e.g., being characteristic for the solutions of rubber and cellulose. If the molecules of high molecular substances possess approximately a spherical shape, then the solutions of such substances have a relatively low viscosity, even in the case of a very high molecular weight.

Examples of this fact are found among the proteins.23

III. Micelle-Colloids.—In this group the colloid particles arise through the association of relatively small molecules. The formation of micelles takes place in the salts of higher molecular acids or bases, for example in the soaps. On account of a one-sided growth of the micelles they are stretched in length. For this reason soap solutions, like those of molecule-colloids, are more viscous. The close relations between the soap solutions and rubber solutions (such as the high viscosity of the solutions, the deviations from Hagen-Poiseuille's law) depend on the same fibre structure of the colloid particles. On the other hand, the internal composition is quite different, since, as has been pointed out, in one case we have to consider micelles and in the other one macromolecules. This is the reason why the subdivision of the solutoidal colloids of Professor v. Weimarn is necessary.

<sup>&</sup>lt;sup>22</sup> Cf. H. Staudinger, Ber., 59, 3029, 1926; ibid., 62, 2893, 1929; furthermore Die hochmolekularen organischen Verbindungen, Kautschuk und Cellulose, published by J. Springer, 1932, p. 140.
<sup>23</sup> See, e.g., G. Boehm and R. Signer, Helvetica chimica Acta, 14, 1370, 1931.

Professor Staudinger further said: According to the observations of Dr. Büchner there is no relation between viscosity and the particle size in the case of cellulose acetates. Büchner's results are in contradiction to my own. The following may be an explanation:

Büchner carried out his viscosity measurements on solutions of equal concentration. Thus, a series of his solutions is much too viscous because they are gel-solutions. Viscosity measurements, in all cases, ought to be carried out below the limiting viscosity, which in the case of cellulose acetates is a specific viscosity of 2.5. It is best to determine the viscosity of solutions of very low viscosity (i.e., with a specific viscosity of 0.2 to 0.5) of representatives of a polymer-homologous series. It is also necessary to determine the degree of dilution to be applied in each case in order to obtain solutions of such low viscosities.

In addition, Büchner has investigated technical products, and these always represent mixtures of polymer-homologue cellulose acetates. In such mixtures the long molecules are distinguished by their high viscosity, whilst they give rise to small osmotic phenomena. Relatively short molecules behave in exactly the opposite way. With such mixtures it is naturally possible that products of equal average molecular weight will possess different viscosities and vice versa.

That the  $K_m$ -constant has been determined correctly is indicated by viscosity measurements with solutions of cellulose-tetraose-acetate, for which I am indebted to Professor L. Zechmeister. On the basis of the viscosity laws, brought out in my lecture, the specific viscosity of a 1.4

per cent. solution of these products is calculated to be 0.070.

H. Freudenberger, at the Chemical Institute of the University of Freiburg, has found it experimentally to be 0.042. The fact that the observed viscosity of this well-defined product agrees so well with the (theoretically) calculated figure demonstrates the correctness of the determination of the  $K_m$ -constant by the experiments of Freudenberger. Furthermore it shows the utility of the relation  $\eta_{\rm sp.}/c = K_m$ . M, where  $K_m = 11 \times 10^{-4}$ , for the determination of molecular weights of cellulose acetates.

**Professor R. O. Herzog** (Berlin-Dahlem) said: The investigations of Dr. Büchner suggest a reference to experiments with different cellulose derivatives which have been going on in our Institute for some time.

Commercial preparations were as carefully as possible separated into fractions according to particle size and the molecular weight of each fraction at different concentrations and in different solvents was investigated by means of the osmometer which has been worked out in collaboration with Mr. Spurlin.

The following table, which was obtained from Mr. Herz, gives an example:—

ACETYL CELLULOSE IN METHYLGLYKOLACETATE AT 53.3° C.

Designation of	Calculated Molecular Weights. Concentration of Solution in Weight Per Cent.									
Fraction.	ı Per Cent.	1/2 Per Cent.	1/4 Per Cent.	1/8 Per Cent.	1/16 Per Cent.					
I B II A3 II A2 III A2 IV A2	27,000 46,000 51,000 75,000 62,000	29,000 45,000 65,000 68,000 72,000	21,000 32,000 58,000 93,000 160,000	30,000 57,000 52,000 110,000 142,000	37,000					

The main part of the preparation consists of fraction II A2 and is The other portions are present in smaller amounts. followed by II A3.

One sees not only that a polymeric homologous series (Staudinger) is present but also that especially the higher molecular portions by low concentrations show a relatively greater osmotic pressure than at the higher concentrations. We hope especially by means of this method to learn particulars about the dependence of aggregation upon chain length,

concentration, temperature and solvent.

Dr. Hirst, in reply, said: Questions have been raised concerning both the structures assigned to the polysaccharides and the methods adopted to determine the chain length of the macromolecules of these substances. The straight-chain formula for cellulose is in accord with the yields of cellobiose obtained on acetolysis, and the work of Freudenberg has shown that the yield of 33 per cent. obtained under certain conditions has no constitutional importance. Difficulties of acetylation of mercerised cellulose appear to originate in surface conditions, as do similar difficulties encountered in the acetylation of other polysaccharides. The fact that methylated cellulose differs in properties from cellulose and cellulose acetate has no structural significance in view of the divergent chemical properties of methoxyl, acetyl and hydroxyl groups.

It is quite possible that application to oxycelluloses of the methods of enquiry now under discussion may yield important results in connection with the degradative oxidation of cellulose, but the question of oxidised derivatives was excluded in the experiments on the chain length of cellulose. At no stage was the material (cotton linters) in contact with oxidising agents, and special emphasis is to be laid on the extremely mild conditions used in preparing the methylated derivative. These were milder than those employed with complete success in the

methylation of sensitive reducing sugars.

Migration of methyl groups does not occur under the conditions adopted for the hydrolysis of methylated cellulose, and the analytical methods were such that accurate estimations of small amounts of tetramethyl glucose in admixture with large amounts of trimethylglucose could be readily carried out. The isolation of 0.6 per cent. of tetramethyl glucose shows that one glucose residue in approximately every 100 differs from the remainder and the properties of cellulose demand that this result be interpreted in the sense that a terminated straight chain of glucose residues is present. Any interpretation which demands the presence of branched-chains is incompatible with the X-ray evidence and with the fact that, in spite of the most extensive researches, no disaccharide other than cellobiose has been detected amongst the acetolysis products of cellulose.

Both with cellulose and with the other polysaccharides examined the methylated derivatives used had been submitted to rigorous fractionation and had been prepared from acetates which in turn had been rigorously fractionated to test their homogeneity. The presence of macromolecules in the form of endless rings admixed with terminated chain molecules is therefore unlikely for cellulose and still more improbable in the case of starch, glycogen and inulin. It may be remarked that if cellulose consisted of glucose residues joined to form endless rings swelling would in all probability be accompanied by

marked longitudinal contraction, which is not the case.

Since demethylation of the stable methyl derivatives cannot be effected without simultaneous hydrolysis of the polysaccharide recovery of the original material after demethylation cannot be used to check the absence of degradation during methylation, but there is much direct evidence that no appreciable break-down takes place. As already mentioned the reaction is carried out under mild conditions and in certain instances has been repeated many times in succession without alteration of the observed chain length. In addition Dr. Machemer has pointed out that in the cellodextoin series, where estimates of chain-lengths have been obtained by independent methods the values found by the chemical method are in excellent agreement with those ascertained by other methods.

It has been suggested that degradation may have taken place during acetylation. Admittedly breakdown occurs when acetylation is carried out by ordinary methods. In the present experiments particular attention was given to the conditions of acetylation and for each polysaccharide evidence was adduced to show that the starting material had undergone no appreciable degradation during acetylation. No attempt was made (as has been erroneously suggested) to deduce the magnitude of the chain length from the properties of the acetates. The estimate of the chain-length is derived solely from the yield of tetramethylhexose obtained on hydrolysis of the methylated polysaccharide.

It seems desirable to affirm the identity of the position now advocated with that advanced by Professor Haworth at York. this is that there is no evidence of appreciable degradation during the preparation of the methylated polysaccharides, and since, for methylated cellulose, the observed chain-length works out at 100-200 glucose residues this value may be taken also as the lower limit for the mean average value of the chain-length of native cellulose. Since, however, a derivative of cellulose obtained by chemical processes was examined, and not the original cellulose, it is possible that the true value for the untreated material may be somewhat, but, having regard to the available evidence, probably not much, higher. It is significant in this connection that the mean molecular weight (30,000) so obtained is in exact agreement with estimates made by three other independent methods, namely, the X-ray method, the ultra-centrifuge method and the osmotic pressure method. Viscosity measurements on native cellulose give higher values which are nevertheless of a similar order of magnitude. Further work to elucidate the discrepancy will be awaited with interest.

As regards the nature of the terminal group at the end opposite to that which gives rise to the tetramethyl glucose, it is certain that in the cellodextrins examined by Haworth and Machemer there are glucose units with free reducing groups. A similar arrangement may be present in cellulose, but serious difficulties are encountered if it is supposed that the molecules of the non-reducing polysaccharides starch and glycogen terminate in reducing groups. Terminated chains are undoubtedly present in these substances, but evidence as to the character of the groups at one end of the chain is at present lacking. Further work is now in progress by which it is hoped to ascertain their chemical nature.

**Dr. Büchner**, in reply, said: The mere fact that the results obtained by the osmotic experiments agree fairly well with those found by several other methods appears to justify the use of the osmotic method. It has a theoretical basis, whereas, on the contrary, Staudinger's viscosity law is a purely empirical one.

It has been observed that the technical products are mixtures.

This, indeed, is probable, but the fact that the molecular weights of many samples are nearly equal, can only be explained if the main part of the substance consist of equal molecules, only small proportions of smaller and larger molecules being present. This seems to be brought out by Herzog's fractionation experiments. Moreover, the same objection may also be raised to the viscosity law, unless it is assumed to be equally valid for solutions of two or more substances.

## ON A SHAKING EFFECT IN CELLULOSE SOLU-TIONS AND OTHER SOLS DETECTED BY MEANS OF TYNDALL LIGHT.

By R. O. Herzog, O. Kratky and E. Petertil.

## Received 29th August.

The present investigation is based on previous observations on solutions of organic compounds of high molecular weight investigated by aid of the depolarisation of Tyndall light.¹ It had been found that in certain solutions—of esters and ethers of cellulose—changes occurred in the course of time which were difficult to explain.

On following up this point we found that solutions of cellulose derivatives, of polystyrol and of other materials show a different angle of depolarisation in those cases where they have been allowed to stand quietly for a long time than the angle observed directly after vigorous shaking.

This shaking effect (Schütteleffekt) is the subject of this paper.

If a parallel beam of natural (unpolarised) light enters a colloidal solution, then the Tyndall light emerging perpendicularly to the direction of entrance is partly polarised, namely perpendicularly to the plane which is defined by the entering ray and the direction of observation. The state of polarisation of the Tyndall light is primarily a function of the particle size, but it also depends upon the form of the particles and the concentration of the colloidal solution. The slope of the function, even in the case of spherical particles, is by no means simple, and it is still less so in the case of non-spherical particles.

According to R. Gans 2 the degree of the polarisation  $\theta$  is given by

$$\theta = \frac{I_n}{I_n},$$

where  $I_n$  is the intensity of the natural, and  $I_p$  the intensity of the polarised part of the diffracted light.

A simple apparatus serves to measure  $\theta$ .<sup>3</sup> The light from an arc lamp passes through a condenser and a filter system into the liquid in the form of a convergent beam; the liquid is contained in a rectangular vessel with plane-parallel walls. The light scattered by the liquid is

Ber., 62, 491, 1929; Eng. Congress Tokyo, Paper No. 11, 1930.
 Ann. Physik, 62, 331, 1920; 65, 97, 1921; Z. Physik, 17, 353, 1923;
 29, 231, 1924.
 B. Lange, Z. physikal. Chem., 132, 1, 1928.

observed by means of a compensation arrangement which allows a direct reading of the angle of depolarisation.

The compounds used were in part natural products and in part synthetic preparations. Those used for the fundamental observations were very carefully fractionated, thus obtaining solutions as homogeneously dispersed as possible. They were chiefly cellulose derivatives and polystyrol, the latter being presented to us by Prof. H. Staudinger, Freiburg, whom we would like to thank for his courtesy. The molecular weights of the latter lie between 4000 and 440,000, those of the acetyl cellulose fractions, which were used especially, between 20,000 and 100,000. The acetyl cellulose fractions were prepared by Frau Deripsko and Herr Herz. The ethyl cellulose preparations were made by Dr. Okamura.

#### General Features of the Measurements.

If the solution of a compound of high molecular weight is shaken in the vessel, together with the air present in this vessel, and investigated in the apparatus previously described, the field of vision of the analyser appears either homogeneous or inhomogeneous. In the latter case, it is interspersed with brighter spots and dark clouds whose movements decrease with growing concentration of the solution; they were still observed not only many hours but even days after the shaking. The adjustment of the analyser in the case of the inhomogeneous field gives rise to some difficulties. However, moments of homogeneity of the field of vision always occur in which the analyser can be adjusted in such a way that the brightness of both halves of the image becomes equal. The arithmetical average of several readings obtained in this way yielded a value of the angle of depolarisation reproducible to  $+ \circ \cdot \circ$ .

If a solution, which, after shaking, appears homogeneous in the field of vision of the analyser, is measured again after standing quietly for several hours, it is found that there is no change in the value of the angle. The intensity of the Tyndall light does not change either. On the contrary, those solutions which show an inhomogeneous field of vision after shaking exhibit, after standing several hours, a lower value of the angle of depolarisation. (This decrease in the angle amounted to as much as 12° in some cases.) At the same time a decrease in the intensity of the Tyndall light can generally be observed. We followed the decrease of the angle of depolarisation in the course of time as it occurs, when the solution, which has been shaken, is left to stand. In every case in which the effect occurs at all we observed an asymptotic fall of the "shaking value" (Schüttelwert) to the "standing value" (Ruhewert). Let us call the difference of these two values the "shaking effect."

The limiting value (standing value) is (practically) reached generally after one to three days, in many cases already after a few hours. The process of shaking the solution again and allowing it to stand gives us essentially the same values as before, so that the process may be considered as reversible, at any rate to a first approximation.

In the case of sols of small elasticity, the effect was found to be independent of the intensity of the shaking; on the other hand, it is strongly dependent in the case of very elastic sols. If the solutions

<sup>&</sup>lt;sup>4</sup> R. O. Herzog and A. Deripasko, Cellulosechem., 13, 25, 1932.

are shaken together not with air but with steel balls, the clouds described above do not occur at all, or only to a very slight extent, that is to say, the field of vision of the analyser is homogeneous. The degree of brightness of the field of vision is intermediate between that of the bright of the dark portions. The phenomenon described here is closely related to thixotropy. B. Lange 5 has shown that the depolarisation decreases when thixotropic CeO<sub>2</sub> gels are liquefied.

## Experiments.

In order to explain this effect experiments were made in which the correlation of the shaking effect to the concentration, the molecular weight and the nature of the solvent was investigated.

Correlation with the Concentration and the Molecular Weight.—On investigating the correlation of the shaking effect with the concentration, it was found that with increasing concentration the shaking effect rose to a maximum at a medium concentration (for example, in the case of acetyl cellulose it lies at ½ per cent.); at larger concentrations the effect generally decreased again. With increasing molecular weight the maximum was shifted towards smaller concentrations.

Correlation with the Nature of the Solvent.—The magnitude of the "shaking value," "standing value" and "shaking effect" is dependent upon the nature of the solvent. Fractions of acetyl cellulose and ethyl cellulose always show a shaking effect if the refractive indices of the substance and solvent are different. When they are equal, or when the difference is very small, the effect disappears. A quantitative relationship between shaking effect and difference in refraction indices does not exist.

The fraction of high molecular weight of polyvinyl acetate (Mowilith HH) shows the shaking effect plainly, while the fraction of low molecular weight (Mowilith H) gives no effect, although in both cases a considerable difference exists between the refractive indices of the solvents used (acetone and butyl acetate) and those of the substances. This is consequently an example of a case in which the absence of the effect is not due to the equality of the refractive indices.

Behaviour in Mixtures of Solvents.—When so much water is slowly added to a solution of Mowilith H in acetone—which, as just remarked, does not show the shaking effect—that a drop which falls into the solution causes a local turbidity, which, however, disappears on shaking immediately, it is found that this solution now shows a marked effect. Thus, addition of non-solvents may cause the effect in those cases where the effect was absent originally.

Distribution of the Substances which Exhibit the Shaking Effect.—The lowest layer of an acetyl cellulose solution which had stood quietly for months was separated from the remaining contents of the vessel by means of careful pipetting, and was investigated separately. It was found that in this portion the effect was absent, while the upper layer and the total contents when mixed again showed the effect.

An experiment with an acetyl cellulose solution which had been centrifuged after the shaking gave a separation of the same kind.

If the angle of depolarisation of a solution which shows the shaking effect is measured at two different heights, it is found, of course, that the number for the "shaking value" in the upper and in the lower half is

<sup>&</sup>lt;sup>5</sup> l.c., p. 20. Compare also K. Krishnamurti, Nature, 124, 690, 1929.

TABLE I.

Substance.	Mol. Wt.	Solvent.	Conc. Per Cent.	Shaking Effect.
Acetyl cellulose D— Fraction B II B .  Fraction M II . Fraction A III M Fraction B II B .	34 000 ,,, 34 300 55 300 74 000 34 000	acetone ,, ,, ,, ,, α-dichlorhydrin	10 A4 H 14 14 14 14	1.0 2.6 1.6 4.9 3.9 0.0 *
Acetyl cellulose H—Fraction B.	26 700	di-acetone-alcohol ,,, methylglykolacetate ,,,	1074 10 14 15 15 15 15 15 15 15 15 15 15 15 15 15	1.8 6.3 6.3 0.9 1.5 2.3 5.4
Fraction IV A2 .	72 500	di-acetone-alcohol  methylglycolacetate	+60 -40 -40 -40 -50 -50 -40 -60 -60 -60 -60 -60 -60 -60 -60 -60 -6	12·5 7·0 2·8 4·4 5·0 7·3 8·9 4·8
Ethyl cellulose O—Fraction C II A .		Carbon tetrachloride butyl acetate benzene		4·7 5·4 o·o *
Polystyrol— Fraction I	4 000 15 000 80 000 200 000 440 000	carbon tetrachloride		0·1 1·0 1·8 1·9 2·3
Polyvinylacetate— Mowilith HH . Mowilith H .	  	butyl acetate "" "acetone acetone with addition of water	10 10 14 14 14 14	2.0 0.0 0.0 3.6
Gelatin Soluble starch . Lamb blood serum		water ,,	To L	4·2 3·8
tech. " Merck " . Mercury sulpho-sali-	_	"	1	4.4
cylic acid †	_	23	1	5.6

the same, while the "standing value" measured after long standing is smaller in the upper half than in the lower half. As can be seen from the following compilation (Table II.) the shaking effect, which is the difference between the "shaking value" and the "standing value," is larger in the upper half than in the lower half of the solution.

<sup>\*</sup> Substance and solvent have the same index of refraction. † For this compound we owe our thanks to Professor Ostwald.

Solution.	τ	Jpper Hal	f.	Lower Half.						
Solution.	S.	R.	E.	S.	R.	E.				
Acetyl cellulose, fraction M II (mol. wt. = 55,300) in acetone ½ per cent	20·0 15·6 16·0	15.1	4·9 4·1 3·8	20·0 15·6 16·0	16·8 13·1 13·1	3·2 2·5 2·9				
per cent	22.0	16.4	5.6	22.0	18.1	3.9				

#### TABLE II.

S: "shaking value." R: "standing value."

E: "shaking effect."

#### Discussion.

Some of the solutions of cellulose-acetate and polystyrol, such as are used in industry, hardly show any effect and some show no effect at all. If, on the other hand, one prepares fractions of approximately uniform molecular weight in the usual manner, there is the distinct shaking effect.

The following is important for the interpretation:

The difference of the effect at different heights after allowing to stand for some time, or after centrifuging, shows that a segregation has taken place; two kinds of segregation are found. In the first place, some parts are deposited, which are visible in the Tyndall-light through their intensive brightness.

Secondly, there is also sedimentation in the main phase, which appears optically homogenous. The difference in composition at different heights arising through this process can be proved not only by the shaking effect, but also quite clearly with help of measurements of the viscosity of solutions (of  $\frac{1}{4}$  to  $\frac{1}{2}$  per cent.) of cellulose-acetate.

We think that it will be necessary to take account of the structure for the purpose of explaining all the observations. In other words, we believe that thixotropic effects play an important rôle. This seems particularly indicated on account of experiments which show a variation of the effect with the duration of shaking.

The experiments are being continued.

Kaiser Wilhelm-Institut f. Faserstoffchemie, Berlin-Dahlem.

## GENERAL DISCUSSION.

**Professor E. Elöd** (Karlsruhe i. B.) said: An analogous case of the alteration of the solubility of large particles by the presence of small particles appears also in fractions of polymerised linseed oil. Fractions of larger particle size, which cannot be dissolved in acetone, may be dissolved again if they are mixed with parts of fractions of small particle size.

**Dr. F. A. Freeth** (*London*) said: Has Professor Herzog ever tried a supersonic (reversed piezo electric effect)?

**Professor Herzog,** in reply, said: The experiments have been started in co-operation with Professor Freundlich of Dahlem.

# RELATIONS BETWEEN THE REFRACTIVE INDICES AND THE BEHAVIOUR OF CELLULOSE FIBRES.

By J. M. Preston, College of Technology, Manchester.

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The early discovery of the significance of the double refraction of cellular structures by Naegeli and, later, its striking confirmation by the results of X-ray spectroscopy is so well known that it requires no description. However, in the past the phenomenon of double refraction has generally been investigated qualitatively rather than quantitatively, and probably because of this the many possible applications of this phenomenon to the investigation of problems of the constitution of fibres have not been appreciated fully.

#### Refractive Indices of Imperfectly Oriented Fibres.

Frey <sup>1</sup> comments on the low values of the refractive indices of regenerated cellulose rayons without offering any explanation, but apart from Frey none of the authors who have reported measurements of the refractive indices of rayons have commented on these very peculiar values. The peculiarity lies in this, that if the regenerated cellulose rayons are really composed of cellulose which only differs from that of the natural cellulose fibres in being less well oriented, then the lower double refraction observed with these rayons should be due to a rise of the lower refractive index  $n_{\alpha}'$  as well as a fall of the higher refractive index  $n_{\gamma}'$ . Now what is actually observed is a fall of both indices, though the higher one falls to a greater extent than the lower one. That a native cellulose fibre does show a rise of the lower index at the same time as a fall of the higher index when it is less well oriented, is seen in the case of cotton, and certain other native cellulose fibres which are

TABLE I.

	<i>π</i> γ.	<sup>11</sup> α·	$n_{\gamma}-n_{\alpha}$	Calculated from $n'_{\gamma}$ . $\theta$ .	Observed $\theta$ .
Ramie and linen .	1.596	1.528	o·o68	,	
	$n_{\gamma}'$ .	n' <sub>α</sub> .	$n_{\gamma}'-n_{\alpha}'$		
Cotton	1·578 1·564 1·559 1·554	1·532 1·531 1·536 1·537	0.046 0.033 0.023 0.017	30·0° 42·7 46·7° 51·3°	24° — —

<sup>\*</sup> Values given by Frey (1).

known to have a spiral instead of a parallel structure, compared to linen and ramie, which have a parallel micellar structure.

It is seen that the value of  $n_\gamma'$  for cotton in the native condition corresponds to a spiral micellar structure which makes an angle of 30° to the fibre axis as was shown by Frey.¹ This is fairly close to the angle directly measured by Balls ² and given in the table above. This angle  $\theta$  can easily be calculated by the application of the ellipse formula. The major and minor axes of the ellipse being given the values of  $n_\gamma$  and  $n_\alpha$  for ramie and flax. The inclination  $\theta$  of the major axis of the ellipse to the fibre axis, corresponds to the inclination of the micellar spiral. Then the polar co-ordinate of the ellipse at the angle  $\theta$  (i.e. in the direction parallel to the fibre axis) is equal to the refractive index parallel to the fibre axis  $n_\gamma'$  and the polar co-ordinate at the angle  $(90 - \theta)$  is equal to the refractive index  $n_\alpha'$ . The relation for  $n_\gamma'$  is as follows:—

$$\cos^2 \theta = 12.01 - \frac{28.05}{(n'_{\gamma})^2}$$
 . . (1)

The value of  $n'_{\alpha}$  is given by

$$\cos^2(90 - \theta) = 12.01 - \frac{28.05}{(n'_{\alpha})^2} \quad . \quad (2)$$

The value of  $\theta$  calculated from the value of the lower refractive index of cotton  $(n_\alpha')$  is  $14\cdot2^\circ$ . In this and other instances to be described later the behaviour of the lower refractive index presents an anomalous behaviour which cannot be satisfactorily explained. The lower refractive index is less affected by the orientation of the structure of the fibres than might be expected from the behaviour of the higher refractive index. The former appears to be influenced by the degree of degradation of the cellulose and under conditions of equal orientation is lower the greater the degree of degradation of the cellulose. It is intended to investigate the behaviour of the lower refractive index in greater detail later, but in the present communication attention will be focussed on the behaviour of the higher refractive index.

#### The Measurement of Refractive Index.

The refractive indices were measured by finding an immersion medium with exactly the same refractive index as the fibres by means of the Becke method  $^5$  and the measurements were made by the light of a sodium flame. In all cases different proportions of two liquids of different refractive indices were mixed till the mixture had exactly the same refractive index as that of the fibres. The media used were phenetole, anisole, ethyl salicylate, methyl salicylate, o-dichlorobenzene, bromobenzene, benzyl benzoate, and acetylene tetrabromide. In each case the fibres were allowed to remain in this immersion medium for twenty-four hours and re-checked before finally accepting the equality of the refractive indices of the fibres and the immersion medium. Subsequently the refractive index of the immersion medium was measured on an Abbé refractometer. All refractive index measurements were made at 21° C.  $n_y$  and  $n_\alpha$  are the maximum and minimum refractive indices of the fibres measured when the light vibrated parallel and perpendicular to the fibre axis respectively.

The value of the double refraction of regenerated cellulose rayons made by the Lilienfeld viscose process is practically the same as that of native cotton fibres, yet both  $n_\gamma'$  and  $n_\alpha'$  are lower in the case of the rayon. Therefore the only satisfactory explanation of the low refractive indices of regenerated cellulose rayons is that the cellulose is not identical with the cellulose of native cellulose fibres. Now the cellulose of regenerated cellulose rayons gives an X-ray spectogram similar to that of mercerised cellulose and different from that of native cellulose. Consequently it was believed that an examination of the refractive indices of mercerised cellulose fibres might provide the clue to the explanation of the values obtained for the refractive indices of rayons. This belief was found to be true and a satisfactory quantitative agreement has been found between certain properties of rayon and mercerised cellulose fibres calculated from their refractive indices and the directly observed values of these properties.

#### Mercerisation.

Linen, ramie, cotton and Lilienfeld viscose rayon fibres were mercerised with and without tension in 18 per cent. NaOH at 21° C. After the NaOH treatment the fibres were washed with very dilute acetic acid, then with distilled water, and finally allowed to dry slowly in the air at room temperature. The mercerisation under tension was carried out by fastening each fibre whilst under a tension of 2 gms. across a glass frame with du Noyer's lanoline cement. It was assumed that ramie and flax fibres mercerised under these conditions, which permit no contraction of the fibres, are still as well oriented after mercerisation as before. The orientation of these fibres in the native condition is known from previous work to be perfect or at least very nearly perfect and so the orientation of these fibres mercerised under conditions which permit no contraction should also be perfect. The observed values of the refractive indices for native and mercerised ramie, flax, cotton and Lilienfeld viscose rayon fibres are given below in Table II.

TABLE II.

Fibre Condition.	$^{n}\gamma$ .	$n_{\alpha}$ .	$n_{\gamma}-n_{\alpha}$ .
Ramie, native and flax, native Flax mercerised, with tension	1·596 1·571	1·528 1·517	o·o68 o·o54
	n' <sub>γ</sub> .	n'a.	$n_{\gamma}'-n_{\alpha}'$ .
Flax mercerised, no tension .	1.556	1.518	0.038
Cotton, native mercerised, with tension mercerised, no tension	1·578 1·566 1·554	1·532 1·522 1·524	0·046 0·044 0·030
Lilienfeld— viscose rayon , mercerised, no	1.559	1.515	0.044
tension .	1.550	1.212	0.035

Mercerisation without tension is seen from Table II. to produce a lowering of  $n_{\gamma}$  and a rise of  $n_{\alpha}$ . If this is due to an increased inclination of the cellulose micelles in the fibre relative to the fibre axis then the lowering of  $n_{\gamma}$  should be a measure of the contraction of the fibre on mercerising without tension.

The average angle of inclination of the cellulose micelles may be calculated for mercerised cellulose in the same manner as the calculation was made above for native cellulose. The values of the major and minor axes of the ellipse to which equations (3) and (4) apply are the values of  $n_{\gamma}$  and  $n_{\alpha}$  for flax and ramie mercerised under tension:  $n_{\gamma} = 1.571$ ,  $n_{\alpha} = 1.517$ .

Then 
$$\cos^2 \theta = 14.86 - \frac{34.21}{(n'_{\gamma})^2}$$
 . . . (3)

and 
$$\cos^2(90 - \theta) = 14.86 - \frac{34.21}{(n'_{\alpha})^2}$$
 . . . (4)

where  $n_{\gamma}'$  and  $n_{\alpha}'$  are the higher and lower refractive indices of the particular fibre under consideration.

Substituting the values given in Table II. of  $n_{\gamma}'$  of the fibres mercerised without tension in equation (3), the average angle of inclination  $\theta$  of the cellulose micelles can be calculated. As the spacing of the glucose residues of the main valency chains maintains a constant value of 10·3 Å per two glucose residues, it follows of necessity that the length of the micelles remains constant. Consequently the length of the fibre after contraction due to increased inclination of the micelles relative to the fibre axis will be proportional to  $\cos\theta$  and the contraction will be proportional to  $\cos\theta$  and the contraction and  $\theta_1$  is the inclination after contraction.

The values given below in Table III. are those for ramie and flax (which give the same values for  $n'_{\gamma}$ ), for cotton and for Lilienfeld viscose rayon. The observed values for the contraction are given for comparison. There will be seen to be a good agreement between the calculated and observed values. The values for cotton and Lilienfeld viscose rayon were determined by a similar technique to that used by Calvert's for cotton hairs. Calvert's values do not correspond exactly as they only apply to the contraction whilst the fibre is still in the mercerising caustic soda, whereas the values required are for the washed and air dried fibres.

Mercerised Without Mercerised With Tension. Calculated Tension. Contraction Observed Fibre. 100. Contracton.  $n_{\gamma}$ .  $\theta_1$ . θο.  $-\cos\theta_1$ ). Per Cent. Per Cent. 34.10 Ramie, Linen . 0.00 1.556 2I 4 1.571 17.2 20·5° 35·6° Cotton 1.566 1.554 12.4 14 Lilienfeld Vis-28.8° 37·8° cose rayon . 1.559 1.550 9.8 IO

TABLE III.

Lilienfeld viscose rayon in its original condition is considered as cellulose mercerised under tension. This has an a priori justification in

the case of all rayon manufactured by the viscose process since the cellulose from which it is made is mercerised during the process of manufacture. Rayons manufactured by the cuprammonium process are not actually mercerised with caustic soda at any stage of the process of manufacture, but the swelling and solvent action of the cuprammonium solution in which they are dissolved during manufacture has a similar action to that of caustic soda in producing a "mercerised" cellulose, as judged by the results of X-ray spectroscopy. The agreement of the calculated with the observed contraction of Lilienfeld viscose rayon confirms this supposition as also do the results for the calculated extensibilities of rayons given below.

#### Qualitative Test for Mercerisation.

The change of the refractive indices of native cellulose on mercerisation can be applied as a test to find out whether fibres of unknown origin are or are not mercerised. Linen, ramie, or other fibres of a similar nature will, if mounted in aniline  $(n_D = 1.587)$  or iso-safrole  $(n_D = 1.58)$  show a higher value of  $n_\gamma$  if in the native state and a lower value if in the mercerised state. This test can be carried out very quickly if the exact refractive index has not, as in this case, to be determined. Similarly cotton fibres if mounted in benzyl benzoate  $(n_D = 1.569)$ , can be distinguished whether they are in the mercerised state or not. In making this test the observations must be carried out by plane polarised light from a sodium flame.

# Extensibility of Cellulose Rayons.

The extensibility of different rayons show very considerable differences, the range being approximately 5 per cent. to 40 per cent. extension at the breaking-point. The explanation of this extraordinarily wide range lies in the variation of the degree of orientation of the cellulose micelles which build up the fibres. The micelles themselves since they consist of main valency chains can be considered as inextensible, and in fact perfectly oriented fibres only show an extension of about 2 per cent. However, if the micelles are not perfectly oriented then extension can take place by the micelles straightening out parallel to the fibre axis. The fibre will thus become progressively better oriented as it is extended till at a stage approximating to perfect orientation the fibre will no longer be able to extend due to the micelles straightening. The angle of inclination of the micelles to the fibre axis will approach zero and consequently  $\cos \theta$  will approach unity. At this stage the fibre will be inextensible and any further stretching will cause it to break. On this hypothesis the extensibility of rayon fibres should be given by the following relation:

Percentage Extensibility at break

$$= 100 \cdot (\cos \theta_1 - \cos \theta)$$
  
= 100 \cdot (1 - \cos \theta) \cdot \cdot \cdot \cdot (5)

where  $\theta$  and  $\theta_1$  are the average inclinations of the cellulose micelles to the fibre axis before extending and at the breaking-point respectively. The value of  $\theta$  can be calculated from the observed value of  $n'_{\gamma}$  by equation (3) above. The calculated compared to the directly measured extensibilities of a number of rayons are given in Table IV. below. There

is a satisfactory agreement between the calculated and observed values except in the case of the Lilienfeld viscose rayon.

The observed extensibilities were measured on 50 c.c. lengths of the rayons which were completely wetted by water before and during the tests.

7	A	B	т	T	T	۲,	,
J.	n	L.	بيد	ند	J.	٧	٠

	Refractive	Indices.	Extensibility.		
Rayon.	n'a.	$n_{\gamma}'$ .	Calculated 100. (1 — Cos θ).	Observed.	
Lilienfeld viscose Cuprammonium I ,,, II Viscose I ,,, III .	1·515 1·518 1·520 1·519 1·519	1·559 1·553 1·549 1·540 1·539	11·5 16·5 22·5 33·5 35·0 41·0	6·6 16·9 25·5 27·2 32·9 39·0	

#### Degree of Orientation of Rayon Fibres.

The average inclination of the cellulose micelles to the fibre axis is given by the calculated angle  $\theta$ . This angle is obviously a measure of the degree of orientation of the fibre, but to express the orientation as the sum of the resolved components of the micelles parallel to the fibre axis compared to the sum of all the micelles the structure of the fibres must be considered in more detail. Preston  $^6$  has shown that the micelles of cellulose fibres occur in swarms which are equally frequently oriented in all directions in the plane perpendicular to the fibre axis and when considering the fibre as a whole that this statistically symmetrical orientation produces the effect of a positive uniaxial crystal. The proportion oriented parallel to the fibre axis will thus be given by  $\cos^2\theta$ : I, instead of  $\cos\theta$ : I as would be the case were the micelles to lie on a perfect spiral. Thus:—

Percentage orientation = 100. 
$$\cos^2 \theta$$
 . . . (6)

TABLE V.\*

Orientation. 100 $\cos^2 \theta$ .	Refractive Index. "\gamma'.	Inclination of Micelles. θ.	Extensibility.	Remarks.
Per Cent.			Per Cent.	The second secon
33.3	1.534	54.7°	42.3	Perfectly isotropic.
40.0	1.538	50.8	36.8	
45.0	1.241	47.9	32.9	Viscose Rayons.
∘ 50.0	1.244	45.0	29.3	
55.0	1.246	42·I	25.8	
60.0	1.249	39.2	22.5	Cuprammonium Rayons.
65.0	1.221	36.3	19.4	-
70.0	I.554	33.2	16.3	
75.0	1.557	30.0	13.4	Lilienfeld viscose Rayons.
80.0	1.560	26.6	10.6	•
85.0	1.563	22.8	7.8	
90.0	1.565	18.4	5·1	
95.0	1.568	12.9	2.5	
100.0	1.571	0.0	0.0	Perfectly oriented.
		<u> </u>	<u> </u>	

<sup>\*</sup> See, however, p. 74.

The corresponding theoretical values of the per cent. orientation, the refractive index (n'), the average inclination of the micelles  $(\theta)$  and the extensibility at break are given in Table V.

The perfectly isotropic state represented by an orientation of 33.3 per cent. parallel to the fibre axis is brought about by an equal frequency of orientation of the micelles in all possible directions. It is thus a statistical isotropy. At any other orientation between this and 100 per cent. orientation, at 60 per cent. orientation (say), the sum of the resolved components of the micelles lying parallel to the fibre axis is 60 per cent., and 20 per cent. each in the two rectangular directions which are transverse to the fibre axis. By the resolved component of a micelle is meant the cosine of the angle of that micelle relative to the particular axis.

# Summary.

- 1. The refractive indices of native, mercerised and regenerated cellulose fibres are quantitatively related to the orientation of the cellulose micelles of which the fibres are built.
- 2. Mercerisation of cellulose fibres produces changes of the refractive indices. The amounts of these changes depend on whether the fibres are mercerised under tension or without tension.
- 3. From the quantitative effect of tension on the change of refractive indices on mercerisation the contraction of fibres mercerised without tension can be calculated.
- 4. The extensibility of regenerated cellulose rayons can be calculated from the refractive indices of the fibres.

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  <sup>5</sup> F. Becke, Sitzungber Akad. Wiss. Wien, 102 (i), 358-378, 1893.
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#### GENERAL DISCUSSION.

Mr. W. T. Astbury (Leeds) said: There are one or two points in this paper about which, if I may, I should like to offer a few suggestions. In the first place, the process of extension in wet rayons cannot be due entirely to rotation of micelles, since, as Professor Mark has pointed out in his paper, by proceeding carefully, extensions of the order of 100 per cent. can be realised, even though the maximum possible by pure rotation is probably something of the order of 57 per cent. (see below). Many silks, both natural and artificial, show almost perfect alignment in their X-ray photographs, yet can yield extensions of at least 20 per cent. Lilienfeld viscose rayon is a case in point. According to Table III., mercerisation under tension still leaves the micelles lying at angles which fall in a cone of semi-vertical angle about 58°. This is a relatively enormous angle of dispersion for which, personally, I have never seen any X-ray evidence. I would suggest that the author, in his study of the refractive indices of fibres, would find it helpful to see how the dispersions given by X-ray methods compare with the results of his own calculations. I think that perhaps he would find the additional data extremely useful in arriving at a sound interpretation of the phenomena of refractive index variation.

In the second place, with regard to the possible extensibility of a perfectly isotropic fibre, that is, one in which the micelles have a random distribution of orientations, even the assumption that the dispersion is confined effectively to a plane gives, not the 42·3 per cent. quoted in Table V., but 57·08 per cent. If the thickness of the micelles is negligible compared with their length, and if they lie originally at angles which fall in a sector of semi-vertical angle  $\phi$ , then the extensibility in this case is:

$$\frac{1 - \int_{0}^{\phi} \frac{\cos \theta}{\phi} d\theta}{\int_{0}^{\phi} \frac{\cos \theta}{\phi} d\theta} = \left(\frac{\phi}{\sin \phi} - 1\right).$$

For random orientation,  $\phi = \pi/2$ , and the extensibility is (1.5708 - 1), or 57.08 per cent.

If the thickness of the micelles is not negligible compared with their length, as is not impossible in the case of artificial silks, a further correction must be introduced, since it is obvious then that the possible extensibility, by micellar rotation alone, can fall to zero.

Professor Van Iterson (Delft) said: I wholly agree with Mr. J. M. Preston as to the importance of the refractive indices for a study of fibres. Applying the Becke method I have determined the two refractive indices for the fibrillae of the cell wall of Valonia utricularis and found I·533 and I·598. These two values do not differ much from the indices calculated (for another species of Valonia), from observations made for the cell as a whole, by W. T. Astbury and they approach very nearly the indices given by A. Frey for pure cellulose fibres. From these facts one may conclude that very probably the fibrils of the walls of these algae are built up from pure cellulose.

However, I feel some difficulties in accepting all the conceptions of Mr. Preston. I only wish here to criticise his paper on one point.

It may be considered as a well-known fact that the micelles in the artificial silks have not the same degree of orientation throughout all the parts of the fibre. At least this holds good for the silks that are not spun under an extra tension. In the outer part of these silk fibres the micelles are almost entirely orientated parallel to the fibre axis; in the inner parts they are orientated at random.

Now by application of the Becke method one obtains the refractive indices for the outer layers of a fibre. It is not possible to determine such indices for the inner parts, when—as is the case with artificial silk—the fibre cannot be squeezed out into fibrillæ.

To apply the formulæ of Mr. Preston one wants to know the *mean value* of at least one of both refractive indices all over the fibre. In my opinion this mean value differs very much from that used by Mr. Preston for his calculations.

When stretching viscose fibres in a wet condition there will be not only an orientation of the micelles in the direction of the stretching, but there will be a gliding too. This is evident from the fact that even the outer layers of the fibres may be stretched over a long distance, for instance, up to 60 per cent., without rupture of the fibres, or without

cracking of the surface. (Mr. Preston calculates the maximum elongation as a percentage of the length of the fibre at breakage; the more common way, followed here, is to give the percentage of the original

length of the fibre.)

**Dr. R. D. Preston** (Leeds) said: The anomalous value of  $n_{\alpha}$  to which the lecturer has drawn attention seems to be very important and quite unexpected, if it is a real effect. In the case of cotton, however, it may be suggested that the anomaly is involved in the structure of the cotton hair, and in the method of measurement of the refractive indices. The cotton hair may be considered as a more or less flattened cylinder; when viewed longitudinally in a microscope it shows, in the centre, two walls superimposed, and, at the edges, a single wall seen in cross-section. If, as in Fig. 1, we insert the traces of the index ellipsoid on these walls, we find, in the centre, two ellipses of axes  $n_{\gamma}$  and  $n_{\alpha}$  one corresponding to the top wall, and one to the bottom. These ellipses are crossed at an angle  $2\theta$ , so that the resultant refractive indices of this compound structure are  $n_{\gamma}$  and  $n_{\alpha}$ . Measurement of each of these would lead to a correct angle of tilt,  $\theta$ . Now the index ellipsoid here involved is an ellipsoid of rotation, and at the edges, where a single

wall is seen in cross-section, the tilt of the ellipsoid is perpendicular to the plane of the field of view. Thus we have a tilt of the index ellipsoid around the smaller axis  $n_a$ . This, therefore, remains unchanged, so that the refractive indices at the edge are  $n_{\gamma}'$  and  $n_{\alpha}$ , the latter being quite unaffected by the spiral tilt. This index  $n_a$  is smaller than  $n_a$ and, using a method of measurement involving phenomena at an edge, it is difficult to see how the measured refractive index could fail to be less than that required to give the true tilt. Even at an

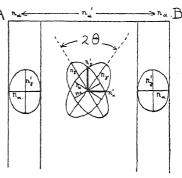


Fig. 1

edge such as AB, we have a transition, more or less gradual according to the degree of flattening of the cotton hair, from  $n_a$ ' at the centre to  $n_a$  at the edges, and if a refractive index were measurable at all it seems certain that it would be less than  $n_a$ '.

It may perhaps be mentioned that we have carried out calculations similar to those of Dr. Preston, in the Textiles Physics Laboratory at Leeds, on a marine alga, *Valonia ventricosa*. These cells are so large that we can dissect and examine a single piece of wall, with no complication of an edge effect. In the single wall itself there occur two series of micellar rows at an angle of about 80°. Both refractive indices here behave in a perfectly normal manner and give the correct angle (80°) as measured by X-rays.

Mr. E. G. Cox (Birmingham) said: The degree of orientation of the micelles is only one of several factors contributing to the observed changes in refractive indices. A theory with any claim to completeness must take into account the variations of both indices; the errors which may arise through making use of variations in  $n_{\gamma}$  only are sufficiently shown by the divergence between the results of Table III. (columns 3 and 5) and those obtained by the much more direct X-ray method.

A factor which is at least as important as micellar orientation is the relative orientation of neighbouring valency chains inside the micelle. Only when the crystalline form in the micelle is the same can the variations in refractive index be attributed with any certainty to variation in micellar orientation. Thus in the case of native cotton (which has the same crystalline form as ramie) the mean spiral angle calculated from both indices is 22°, differing by only two degrees from the value directly measured by Balls. Even in this case, however, the effect is due to the spiral structure which is not the same thing as imperfect alignment of the micelles. If there is any change in the relative orientation of the cellulose chains, the interaction between hydroxyl groups on neighbouring chains is considerably altered, giving rise to large changes in the refractive indices. The difficulty of correlating the optical properties and molecular orientation of crystalline sugars is well known, and is undoubtedly due to the preponderating effect of the hydroxyl groups. In the case of native cellulose, its insolubility and other properties point to strong lateral association of the chains of glucose residues; this association takes place through hydroxyl groups and will give rise to comparatively high refractive indices. The treatment which the material undergoes during the manufacture of rayon breaks down the association between the chains with the result that both indices are reduced. Coupled with this is a certain loss of micellar alignment which tends to reduce  $n_r$  and raise  $n_a$ . The net result is that both are decreased but  $n_{\nu}$  more than  $n_{\alpha}$ .

The fact that intra-micellar phenomena play a very large part in determining the optical properties is very well shown by the case of nitro-cellulose. If the optical properties are ascribed solely to micellar orientation then all reasonably well oriented fibres should show positive double refraction. Actually fully nitrated cellulose fibres show negative double refraction (i.e., the transverse refractive index is greater than the longitudinal); since it gives a normal fibre photograph this phenomenon must have a purely intramicellar origin.

Mr. J. M. Preston (Manchester), in reply, said: My paper was designed primarily to describe a new method of investigation of cellulose fibres and the effects of "activation" and degradation. I consider my treatment to be a first approximation only to the solution of what is a complex

problem.

With regard to Dr. Astbury's remarks that almost perfectly oriented Lilienfeld viscose rayons can have extensions of "at least 20 per cent." A characteristic of this rayon is its small elongation, which is of the order quoted in Table IV. above. It should be made clear that my remarks about the small elongations of perfectly oriented fibres were limited to cellulose fibres. Further, extensions of 100 per cent. for cellulose fibres are only possible after treatment with powerful swelling and plasticising media such as concentrated sulphuric acid.

As a consequence of Dr. Astbury's criticisms I have re-examined my expression for the percentage orientation, and I find that its theoretical validity cannot be defended, therefore I desire to withdraw expression (6) and column I of Table V. above. Further, the "perfectly isotropic" state corresponds to an inclination ( $\theta$ ) of 60° and not 54.7° on the assumptions contained in my paper, and a top line should be inserted in Table V. reading  $n_{\gamma}' = \text{I} \cdot 530$ ;  $\theta = 60^{\circ}$ ; extensibility = 50.0 per cent.; perfectly isotropic. However, a criticism can be applied to the expression

quoted by Dr. Astbury which is based on that of Poole.<sup>1</sup> Dr. R. W. Guelke and I have made a theoretical analysis of the problem on Poole's

assumption as follows:—

Poole's expression implies that all angles of inclination of the micelles to the fibre axis are considered equally probable. This is only true if all the micelles lie in a plane containing the axis, and if the integration as quoted by Dr. Astbury is only extended over this plane. On the other hand, when a three-dimensional random orientation is considered, the probability of a micelle occurring in the interval  $\theta - (\theta + d\theta)$  relative to the axis is  $\sin \theta \cdot d\theta$  and the integral on Poole's assumptions then becomes:

$$\frac{1 - \int_0^{\pi/2} \sin \theta \cdot \cos \theta \cdot d\theta}{\int_0^{\pi/2} \sin \theta \cdot \cos \theta \cdot d\theta}.$$

This is equal to I or 100 per cent. extensibility, and not 57 per cent. There is good reason to believe that this expression is only true in strongly swelling and plasticising media, and therefore is not directly applicable to the ordinary wet and dry extensibilities of cellulose rayons.

The difference between the treatments which give rise to the two expressions for extensibility on Poole's assumptions is briefly, but in rather more detail, as follows: if the micelles are all in one plane, the probability of finding a micelle in the interval  $\theta - (\theta + d\theta)$  is  $d\theta/\pi^2$ ,  $d\theta$  being a line element of the arc of the circle and  $\pi/2$  being the length of the arc or  $\int_0^{\pi/2} d\theta$ . The contribution of each micelle is calculated as  $l \cdot \cos \theta$  by Poole and the total length contributed by all the micelles of a random orientation as:

$$\frac{\int_0^{\pi/2} l \cdot \cos \theta \cdot d\theta}{\pi/2}.$$

From this Astbury by assuming the fibre to be capable of extending until the micelles are pulled parallel to the axis obtains the extensibility as:

$$\frac{l - \int_0^{\pi/2} \frac{l \cdot \cos \theta \cdot d\theta}{\pi/2}}{\int_0^{\pi/2} \frac{l \cdot \cos \theta \cdot d\theta}{\pi/2}} = \frac{I - \int_0^{\pi/2} \frac{\cos \theta \cdot d\theta}{\pi/2}}{\int_0^{\pi/2} \frac{\cos \theta \cdot d\theta}{\pi/2}},$$

On the other hand, in order to obtain an expression for the extensibility of a random orientation in three dimensions, it is necessary to consider a surface element on a sphere instead of a line element on a circle. The area of the former element is  $d\theta \cdot \sin \theta \cdot d\theta$ , where  $\theta$  is the angle of the micelle to the fibre axis (the complementary angle to the "latitude") and  $\phi$  is the angle subtended at the equator (the "longitude").

The probability of a micelle occurring in the surface element  $d\theta$ .  $\sin\theta$ .  $d\phi$  is:

$$\frac{d\theta \cdot \sin\theta \cdot d\phi}{\int_0^{\pi/2} \int_0^{\pi/2} \sin\theta \cdot d\theta \cdot d\phi} = \frac{\sin\theta \cdot d\theta \cdot d\phi}{\pi/2}.$$

<sup>&</sup>lt;sup>1</sup> Trans. Far. Soc., 21, 127, 1925.

In order to obtain the probability of a micelle occurring in the interval  $\theta - (\theta + d\theta)$ , it is only necessary to integrate  $\phi$  in the last expression from  $\theta$  to  $\pi/2$ , which gives:

$$\int_0^{\pi/2} \frac{\sin \theta \cdot d\theta \cdot d\phi}{\pi/2} = \sin \theta \cdot d\theta,$$

instead of  $\frac{d\theta}{\pi/2}$  if the micelles had all been in one plane.

Substituting  $\sin \theta \cdot d\theta$  for  $\frac{d\theta}{\pi/2}$  in Dr. Astbury's expression the extensibility is given by:

$$\frac{1 - \int_0^{\pi/2} \sin \theta \cdot \cos \theta \cdot d\theta}{\int_0^{\pi/2} \sin \theta \cdot \cos \theta \cdot d\theta} = 1.$$

The very low almost constant value for  $n_{\alpha}$  for cellulose rayons has already been reported in the literature on several occasions.<sup>2</sup>

Mr. R. D. Preston's explanation of the behaviour of the lower refractive index  $(n_{\alpha}')$  is probably the correct one and might possibly be extended to the case of rayon fibres since the micelles in the surface layer are probably tangential to the surface.

The explanation of the divergence of the calculated inclination of the micelles from  $n_{\gamma}'$  and  $n_{\alpha}'$ , commented on by me and by Dr. Cox, may be contained in Mr. R. D. Preston's remarks.

It is of interest in relation to the changes of refractive index produced in native cellulose by mercerisation and conversion into rayon that Kirchhof <sup>3</sup> found that oxidation and depolymerisation of rubber produced changes in the refractive indices of rubber of the order of a few units in the third decimal place.

Mr. W. T. Astbury (Leeds) (communicated): The main object of my comments on Mr. Preston's paper was to emphasise the particular value of X-ray methods in the study of the optical properties of fibres, because I feel sure that the author would find them of very great help in all questions of orientation and extension. But I see from Mr. Preston's reply that I was not sufficiently explicit or comprehensive in my remarks, so it may not be out of place here to amplify them somewhat. As he points out, the expression

$$E = (\phi/\sin\phi - 1),$$

leading to a maximum extension of 57 per cent. when  $\phi=\pi/2$ , is based on integration over a plane only, whereas the maximum extension for a perfectly random distribution in space is I or IOO per cent. In this latter case the unstretched length is

$$\int_0^{\phi} \frac{\sin \theta \cos \theta \, d\theta}{(1 - \cos \phi)},$$

and the general expression becomes

$$E = \frac{(\mathbf{I} - \cos \phi)}{(\mathbf{I} + \cos \phi)},$$

$$(\mathbf{I} - E)$$

or

$$\cos \phi = \frac{(I - E)}{(I + E)},$$

<sup>2</sup> A. Herzog, Kunstseide, 13. 6, 1931; J. H. Skinkle, J. Text. Inst., 23, T<sub>75</sub>, 1932.

<sup>8</sup> Kautschuk, 8, 137-142, 1932.

both forms of which are very convenient to remember. (When  $\phi = \pi/2$ , E = I.)

We have thus now expressions for two limiting cases, the second of which certainly refers only to jellies or heavily swollen fibres, as Mr. Preston points out. I think that probably the first expression is more valid for natural fibres and at least the outer layers of artificial fibres, but in any case, the point I specially want to make is that the region over which the integration must be carried out can in general be determined directly by X-ray analysis. From a series of photographs of the fibre at various inclinations to the X-ray beam it is possible to plot out on a sphere the loci of the normals to the various crystallographic planes the "pole figure," as it is called—and to deduce therefrom the actual dispersion in any direction in space. When this has been done, the integration must obviously be carried out over the regions so obtained. whatever their shape. A similar integral also controls the optical properties, of course, and it is clear that each individual case demands its own special treatment. As typical examples of dispersions that are confined more or less to what is effectively one plane, I may quote the quills of feathers, the finger nails, the cutis vera of the skin, and cellophane films.

Mr. J. M. Preston, in reply (communicated): I am glad that Dr. Astbury agrees with my treatment, on Poole's assumptions, of the extensibility of completely randomly oriented fibres. His opinion of the utility of the X-ray method is mine also and, in fact, I had used comparative tests by X-ray and optical methods in an earlier paper which dealt with the relation between the dichroism and orientation of fibres.

# THE STRUCTURE OF XEROGELS OF CELLULOSE AND DERIVATIVES.

By S. E. SHEPPARD.\*

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The term "xerogel" is a useful one connoting colloids in a relatively dry state, that is, substantially free from liquid and volatile dispersion media. It comprises such natural colloids as cotton, wool, silk, hair, horn, such partial artifacts as gelatin, leather, charcoal, and cellulose derivatives (esters, ethers, etc.), and such completely synthetic products as phenol-formaldehyde resins, silica gel.

This paper deals solely with the xerogels of cellulose and certain derivatives, chiefly esters. It summarises briefly experimental results and conclusions therefrom obtained over several years by the author

and several collaborators.

# Methods of Investigation.

The materials in question, e.g. cellulose fibres, regenerated cellulose sheets or films, cellulose nitrate sheets and masses, "precipitated" cellulose esters, obviously have not external crystalline form, excluding,

<sup>\*</sup> Communication No. 504 from the Kodak Research Laboratories.

therefore, conventional crystallographic examination. Though amorphous in this sense, they are known to possess a fine structure showing more or less definite approach to crystallisation of particular units (crystallites) on X-ray examination. This approach is generally most marked in definitely fibrous materials, and the X-ray attack becomes increasingly valuable. However, by the nature of the case, it allows conclusions chiefly as to the more or less orderly packing, or spatial arrangement, of atoms in molecular units. It can, it is true, give some information as to the average size of eventual crystalline units (crystallites) built up of these, but in any case little information as to how these are joined together. It is unnecessary to dilate on the evidence from X-rays for the "long chain," primary valence chain, or macromolecule of anhydroglucose units as the "fine" structure element of cellulose. We may accept provisionally the primary chain:

That is, a chain of cellobiose units, of unspecified length, and unspecified terminal groups or connections.

Ultra-violet microscopy and dark field (ultra-) microscopy can give valuable information, particularly on thin films and sections.<sup>2</sup> It has served so far chiefly to confirm or refute optical homogeneity of certain thin films, of which more later.

The application of electron (and atomic) diffraction to these materials is in its infancy. This also is restricted to "thin films"; the early results of Taylor-Jones 3 on cellulose nitrate have not been entirely confirmed.4 In any case, the formation and structure of "thin films" approaching molecular thickness, interesting and important, cannot replace entirely the examination of more massive systems—where the units have a lower degree of freedom. In this field, we have found the study of the sorption of gases and vapours by cellulose and its derivatives of great value. One may divide this into three parts:-

- i. Statics of sorption, i.e. adsorption and desorption isotherms.
- ii. Kinetics of sorption, i.e. velocities of sorption and transpiration of gases and vapours.
- iii. Energetics of sorption, e.g. heats of sorption.

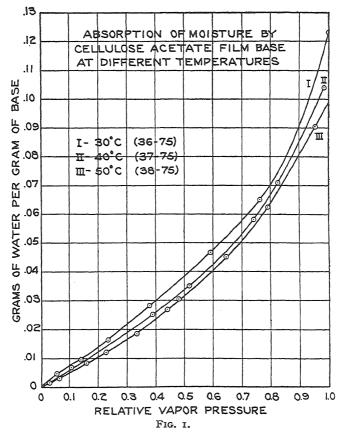
Before passing to particular results in this field, we may note as further means of study of more massive—i.e. definitely three-dimensional pieces—the study of birefringence (natural and induced double refraction), of elastic properties, and of electric properties.

<sup>&</sup>lt;sup>1</sup> Cf. K. H. Meyer and H. Mark, "Der Aufbau der Hochpolymeren Organ. Naturstoffe." Akad.-Verlag, Leipzig. 1930.
<sup>2</sup> H. Zocher, Naturwiss., 17, 672, 1930.
<sup>3</sup> E. Taylor-Jones, Phil. Mag., 12, 641, 1931.
<sup>4</sup> J.-J. Trillat (To be published).

## Sorption Statics.

Sorption isotherms for water vapour with cellulose and derivatives were determined with a modified McBain-Bakr sorption balance. Typical adsorption isotherms of a cellulose acetate (about 40 per cent. acetyl) are shown in Fig. 1.

It should be noted that the values at any point on such adsorption, or on desorption isotherms with cellulose and its derivatives are stationary end values, not final equilibrium values. In other words, there is considerable hysteresis in the adsorption-desorption cycle. The magnitude of this is reduced by repeating the sorption-desorption cycle, more



so for evaporated films of cellulose esters than for coagulated or precipitated material.

We were unable to eliminate completely the sorption hysteresis by repeated evacuation to 0.005 mm. pressure, at the highest temperatures the material would permit. This hysteresis appears to be a characteristic of the incompletely rigid (imperfectly crystalline) structure of these gels.

The sorption phenomena with water vapour of cellulose show several other significant features:

<sup>&</sup>lt;sup>5</sup> S. E. Sheppard and P. T. Newsome, J. Phys. Chem., 33, 1817, 1929.

(a) The sorption for mercerised, washed cellulose, and for celluloses regenerated from cuprammonium, viscose, cellulose esters, is fairly constant for these materials, and uniformly higher than for "native" cellulose. This is illustrated by the following table (Table I.):—

Standard	Standard Cellulose. Cotton Linters.		Hydrate Cellulose.		Hydrate Cellulose. B.		Hydrate Cellulose.		
<i>p</i> / <i>P</i> .  o.	z/m. 0.	<i>₱</i> / <i>P</i> .	x/m. 0.	⊅ P. o.	x/m. 0.	⊅/P. o.	x/m. 0.	р/Р. о.	x/m. 0.
0·027 ·116 ·266 ·497 ·669 ·809 I·coo	0.0029 .0162 .0290 .0458 .0603 .0806 .1751	0.059 .162 .300 .463 .609 .828	0.0107 .0191 .0290 .0401 .0519 .0870 .1497	0.030 .091 .175 .378 .584 .678 .816	0.0056 .0156 .0296 .0552 .0808 .0964 .1245 .2269	0·062 ·150 ·378 ·591 ·875 1·000	0·0057 ·0137 ·0621 ·0998 ·1635 ·2347	0.062 -169 -325 -509 -681 -864 1.000	0·0163 ·0370 ·0636 ·0894 ·1187 ·1702 ·2657

TABLE I.

Hydrate cellulose A was from mercerised washed linters, B from cuprammonium, C from hydrolysed cellulose acetate—(reprecipitated from solution).

It is known that all these hydrate celluloses give a similar X-ray diagram, differing from that of "native" cellulose in that the basis cell shows slight contraction in the fibre direction, and dilation in two directions at right angles.

#### Nature of Water Vapour Sorption.

For reasons to be mentioned, it is certain that the sorption of water by cellulose is connected with the latter's hydroxyl groups. If each — OH in cellulose held only one water molecule (by dipole orientation) cellulose could take up some 33 per cent. water, whereas even hydrate cellulose takes up only some 23 per cent., native cellulose about 16 per cent., at saturation at 25° C. Moreover, from the shape of the adsorption curves and from the variation of the heat of adsorption with per cent. water regained, it is certain that a considerable part of this water is held by much weaker constraints than that first adsorbed at low vapour pressures.

X-ray examination shows that water molecules do not penetrate the crystallites, to alter the basis cell.\* The sorption is therefore not intramicellar, but intermicellar, to use the terms proposed by Katz.

The primary process appears to be attachment of water molecules to — OH groups exposed on the surface of the micelles in intermicellar spaces. This is probably monomolecular.

K. H. Meyer and H. Mark <sup>6</sup> point out that assuming micellar dimensions of bundles of 40 to 60 glucosan chains, about half the hydroxyls available would lie on the surface of the micelles, the other half inside. These latter would be strongly engaged in ensuring the cohesion of the

6 Op. cit.

<sup>\*</sup> Distinction from the solvation of cellulose by cuprammonium, and of cellulose esters by organic solvents.

crystallite. But again, not all of the micellar surface hydroxyls could be free to sorb water molecules, otherwise water would probably peptize cellulose to a colloidal solution. (The peptization by saturated solutions of thiocyanates, etc., does perhaps depend upon the dissolution of micellar surface hydroxyl couplings.) However, the lowering of tensile strength and rigidity of cellulose fibres and films by water sorption may be proportional to the amount of directly polarised water molecules. At present it does not appear probable that much more than about 5 per cent. water is held by primary sorption to hydroxyls by native cellulose, nor much more than 7 per cent. by hydrate cellulose. These are the amounts retained at  $p/P_s = 0.5$ ; for values lower than this, the pore radii necessary for capillary condensation of water soon become meaningless.

On the other hand, the bulk of the water adsorbed at higher vapour pressures is probably held by capillary condensation, and in intermicellar spaces of the order from 15 Å.U. up to 500 Å.U., but with very few above 200 Å.U.

#### Esterification and Etheration.

The fundamental importance of the OH groups for sorption of water is shown by the reduction of sorption by esterification and etheration of the hydroxyls. For example, the water sorption of cellulose is progressively reduced with degree of acetylation, and, in fact, for fibrous non-hydrate (native) cellulose, from about 16 per cent. at saturation to 9 per cent. for triacetate (44.5 per cent. acetyl). Cellulose acetates of less than 44.5 per cent. acetyl have different water sorptions, according as the hydrate or the native lattice structure is present, the former showing considerably higher sorption than the latter.

The fact that cellulose triacetate, in which all the hydroxyl groups have been acetylated, still shows a relatively high water absorption, appears puzzling in view of the fact that the water absorptions of cellobiose octacetate and glucose pentacetate are extremely small—less than I per cent. at saturation. It appears that this adsorption must be credited chiefly to capillary condensation in micropores. This is borne out by the fact that incorporation in a cellulose acetate sheet of phlegmatic (high boiling) non-solvent liquids, such as dibutyl phthalate, can lower the water adsorption to a half of its original value. Such liquids, which must wet the cellulose ester, are displacing water in the intermicellar spaces.

#### Molecular Weight of Ester Group.

The molecular weight of the ester group also affects the sorption of water. If a series of esters of equivalent degree of esterification—preferably as triesters—but increasing M. W. of acyl group from formyl H—CO— to stearyl  $CH_3(CH_2)_{16}$ —CO—, are compared for water sorption it is found that the water sorption steadily falls with increasing M.W. of the acyls. For cellulose triacetate, at  $p_s$  at 30° C. 10 per cent., for tripropionate 2 to 3 per cent., tributyrate 1.8 per cent., trivalerate about 1.6 per cent., tristearate about 1 per cent. The significance of these results seems to be that the increasing alkyl chains tend to act like the just mentioned phlegmatic liquids, in displacing water molecules from the intermicellar spaces. It will be noticed that the fall in water sorption is very rapid from cellulose to the tripropionate, from then on much

less pronounced. This has considerable resemblance to the elastic properties, which also show a sharp fall (tensile strength) to the propionate, with subsequent more gradual decline to the stearate.7

## Sorption of Alcohols.

If we assume that sorbable type molecules, i.e. having an active polar group of increasing M.W., experience increasing difficulty in navigating the intermicellar spaces, then experiments with a homologous series of alcohols might throw some light on the magnitude of these. Accordingly, sorption experiments were run on alcohols from methyl to n-octyl, using a series of cellulose acetates of different acetyl contents as adsorbents. Disregarding for present purposes the effect of acetyl contents, the most significant results were :-

The molar adsorbing capacity of a secondary cellulose acetate (39 per cent. acetyl) contrary to the behaviour of primary (fibrous) acetates did not fall in a quite regular way on passing to the higher alcohols. Approximately, however, the molar adsorption fell rapidly from water to butyl alcohol (4 C-atoms) and then remained constant at about 0.004 to 0.005 moles per gram acetate. This saturation value may be regarded as characterising the "outer" surface—which is by no means the same as the geometrical surface, because including all sub-microscopic contours and rugosities. It is what would be expected for approximately monomolecular adsorption, with the hydroxyls of the alcohols oriented to the cellulose, the cross-section of the alcohol molecules remaining the same. According to N. K. Adam 8 the area of the oriented—CH2OH group is  $21.7 \times 10^{-16}$  cm.<sup>2</sup> With 0.0045 moles of adsorbed alcohol, the total area occupied would be  $0.0045 \times 6.06 \times 10^{23} \times 21.7 \times 10^{-16}$ , that is, 0.6 × 107 cm.2 per gram. Kalberer and Schuster 9 assuming monomolecular adsorption of SO2 to native (cotton) cellulose calculated an "inner" adsorbing surface of 107 cm.2 per gram. This was much larger than that found by F. Paneth 10 from dye adsorption, viz., 104 - 105 cm.2 per gram.

The value calculated from the (higher) alcohol adsorption at saturation pressure is almost certainly too large, since there is undoubtedly some degree of capillary condensation. At  $p/P_s = 0.5$ , however, when the adsorption is about half that given, the capillary condensation would be nearly negligible since the pore radius required (10 Å.U. and less) could not accommodate droplets of alcohols of C8 atoms, i.e. about 12 A.U. in length. Hence, a more probable value would be 0.3 × 107 cm.2 per gram for the precipitated acetate. As this was near a "diacetate" in composition, assuming orientation to - OH groups of the cellulose body, the adsorption area calculated for cellulose would be about three times as great, or about that calculated by Kalberer from SO, sorption. It may be noted that a film 3/1000 inches thick of this same acetate, coated from acetone solution gave about one-tenth the value of the precipitated material. This is in marked contrast to the sorption of water vapour, where the sorption, was largely independent of the form of the material. It confirms the view that the adsorption of the higher

<sup>7</sup> Cf. M. Hagedorn and P. Moeller, Veröffentl. wiss. Zentr. Lab. Cl. photogr.

Abteil. Agfa, Vol. I., p. 149, 1930.

8 N. K. Adam, "Physics and Chemistry of Surfaces." Oxford, 1930.

9 Cf. Meyer and Mark, op. cit., p. 125.

alcohols is not effected in the intermicellar spaces. Incidentally, determination of the "density" of these materials in different liquids confirms this result, water giving much the higher value.

# Sorption Kinetics and Transpiration.

Attempts to apply the Fick diffusion law to the rate of sorption of water vapour by films of cellulose esters about 5/1000 inches showed that this is only followed after an initial period of I to I·5 hours. We may assume an initial sorption and condensation process in the surface layer, followed by a slower penetration (diffusion) process through the mass. This appears to be in agreement with measurements of the rate of transpiration of water through these films. There is usually an initial lag or induction period—up to an hour—after which a constant amount per unit time transpires.

With films of cellulose esters coated from solutions in acetone or other volatile solvents, the rate of transpiration of water was independent of the hydrostatic head, indicating that no true capillary canals existed—whereas such capillary canals are present in the liquid-containing organogels <sup>11</sup> and in the membranes prepared for ultrafiltration. If originally present prior to complete evaporation they must become sealed on drying.

There do exist, however, capillary ducts or pockets of greater dimensions on the side where evaporation occurred than on the side adhering to the support. This is shown by the reduction of sorption produced by sealing this side. Opaque, meerschaum-like films produced by evaporating from acetone in presence of water vapour have the larger capillary pockets (r about 1000 Å.U.) also on the outer side only—they do not extend through the film.

#### Heats of Sorption.

Calculations of the heats of sorption of water vapour (from sorption isotherms at different temperatures) for cellulose (cotton linters) are quite consistent with the view that primary sorption, at lower vapour pressures, is a chemo-sorption of water molecules to — OH groups, superposed on which occurs a capillary condensation. With cellulose acetates, the integral heat of adsorption of water vapour approaches rather closely to the mere "heat of condensation," and much more so for triacetate than for a "diacetate." This indicates that with the triacetate the sorption of water is almost entirely by capillary condensation.

# Structure Revealed by Birefringence.

Although visibly "amorphous," the cellulosic xerogels are not isotropic. Ambronn's studies of birefringence of natural fibres showed this for cellulose itself. The fibres of articial silks, the sheets of cellulose esters by evaporation of solvents, are also optically anisotropic.

Isotropic films can be obtained by careful evaporation on a mercury surface. In this case the units of the solution are free to orient in any direction, and a random aggregate results. Films obtained by evaporation of solvent from solutions on solid supports give *uniaxial* layers. If such sheets are *swollen* in a mixture of solvent and non-solvent (e.g.

<sup>&</sup>lt;sup>11</sup> Cf. K. Klemm and L. Triedman, J. Amer. Chem. Soc., 54, 2637, 1932.

acetone-water) and dried while stretched in one direction then pronouncedly biaxial layers are obtained.

These results by optical examination <sup>12</sup> are confirmed by X-ray examination. <sup>13</sup> They show that in these xerogels there is orientation of certain anisotropic units produced in the processes of congelation

and drying.

If we provisionally term these units "micelles," then in the isotropic films their axes are at random, in the uniaxial sheet they lie parallel to the flat surfaces, but at random otherwise, while in the biaxial films the axes of the micelles are oriented in the direction of the tension applied during drying. These investigations do not indicate whether the anisotropic units of these xerogels are the original "crystallites" of the native fibres, micelles produced by "recrystallisation" from solutions, or the chain-like macromolecules of cellulose.

An investigation in this laboratory of the spreading of cellulose esters on mercury (from solutions) established the formation of "molecular" films from rather dilute solutions. Results of the same import were obtained independently by Katz and Sanwel, and the optical homogeneity of the films was confirmed by Zocher. X-ray diffraction studies by K. Hess and collaborators have shown that in swelling and solution of cellulose esters there occur lattice distention and eventual disruption, with change of lattice type on re-formation of the xerogel by precipitation or drying. Formation of molecular compounds between the solvent and cellulose ester (hexose units) was indicated; this was shown for camphor: cellulose nitrate by elastic measurements also by Sheppard and McNally.

Where true intramicellar swelling by a solvent occurs therefore it is probable that in solution the original micelle is penetrated and largely disrupted by solvent molecules. On cooling to organo-gel formation, on precipitation by non-solvents, or on evaporation, micelles are regenerated, but frequently with an altered lattice structure. The mechanical or elastic structure of the resulting xerogel is determined not only by tensions and adhesions produced mechanically in coagulating or drying, but also by molecular orientations of the cellulose atom groups (— OH groups, acyl groups, etc.) to atom groups of the solvent.

N. K. Adam <sup>14</sup> has pointed out that "cellulose trilaurate gives a film [thin] closely resembling the 'expanded' films of trilaurin; cellulose tristearate a condensed film like tristearin, with area only slightly greater than that appropriate to three long chains closely packed. Evidently when the long chains attached to the hydroxyl groups on the carbohydrate parts of the cellulose molecules become long enough, they dominate the character of the [thin] film, and determine the arrange-

ment and packing of the molecules."

But what is said here of the thin, molecular films appears to hold in large degree for the thicker sheets and filaments. The progression of properties of the xerogels of the cellulose esters of aliphatic acids with increasing molecular weight of the acids shows equally that as the hydrocarbon chain increases it dominates "the arrangement and packing of the molecules." There is, therefore, a high probability that the micellar build of these xerogels is predetermined by molecular orientations in the solutions, rather than by re-aggregation of the micelles of the original fibres.

 <sup>&</sup>lt;sup>12</sup> Cf. J. G. McNally and S. E. Sheppard, J. Phys. Chem., 34, 165, 1930.
 <sup>13</sup> J. J. Trillat, J. d. Phys., 2, 65, 1931.

In agreement with this is the fact that one and the same cellulose ester (e.g. acetate) dissolved in different solvent combinations can give either brittle or flexible films on drying, and the transition is entirely reversible.

In conclusion, my thanks are due to several collaborators, and particularly to Dr. J. G. McNally, Dr. P. Newsome and Mr. S. S. Sweet.

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# RESEARCHES ON THE CHANGE IN THE LATTICE OF NITROCELLULOSE.

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Nitrocellulose has been the object of much recent research, based principally on X-ray diagrams. Just lately a very interesting paper of Trogus, Hess and Katz <sup>1</sup> has shown that the fibres of nitrated ramie, at the maximum, swelled in certain mixtures of organic liquids (methanol-cyclohexanone, for example), and then examined by X-rays, showed an important change in the position of the crystalline interferences; in proportion as the liquid mixture evaporates from the fibre we recover, little by little, the unaltered diagram of the original fibre; so that we have here a phenomenon which is reversible.

The above-mentioned authors conclude that it must be admitted, for certain swelling media, that there is a combination between the cellulose and the medium (a compound doubtless analogous to a dissociable hydrate); we have in fact found that this is what does take place in the case of nitrocellulose and camphor <sup>2</sup> and it probably takes place in the case of many plasticisers or solvents. It is our intention in this paper to review rapidly the researches we have carried out in the Kodak-Pathé laboratories in Paris.

#### Conversion of Fibrous Nitrocellulose into the Condition of Film.

It is interesting to see what happens when we do not limit ourselves to a single swelling, but proceed up to the stage of complete dispersion, followed by evaporation of the solvents with formation of a film. We have done this when working with nitrated cotton (12.95 per cent., approximately trinitrocellulose) using as solvent pure acetone and evaporating to the form of a film.

We used very fine collimators (0.3 mm. diameter) permitting a good separation of the different interference bands; the fibre or the film was examined with the  $K_{\alpha}$  rays of copper, using a thickness of 0.3 mm.

We ascertained, then (Figs. 1-6), that the diagrams of nitrated cotton and of the corresponding film are different; the difference con-

<sup>&</sup>lt;sup>1</sup> Z. physik. Chem., **7B**, H. 1, 1930. <sup>2</sup> J. J. Trillat, Compt. rend., 654, 1930.

sists essentially in the appearance of new Debye-Scherre rings corresponding to large spacings. As this phenomenon depends upon the solvent used as well as upon the degree of drying of the film, we shall examine it in greater detail in the following paragraph; we may now say simply that the film obtained, for example, by evaporation of an acetone solution of nitrated cotton (12.95 per cent. N) is crystallised (Fig. 1). This is in accord with what is known as to the structure of cellophane films, which also appears to be crystallised with a structure different from that of the initial cotton (hydracellulose in place of cellulose). The fact that we pass from the phase of dispersion brings about a change in the lattice corresponding to a new form of the cellulose; this is produced also in the case of nitrocellulose in the region of the maximum of nitration. This shows the generality of these phenomena of transformation of the lattice, even when we study the cellulosic derivatives in the form of films.

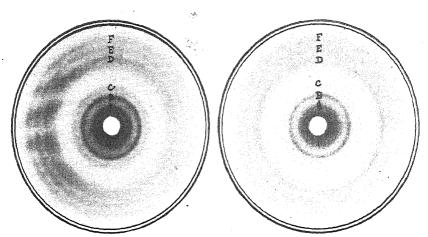
If now we repeat the same experiment with less nitrated cottons (12-10 per cent. N) we establish that while the fibres still retain a crystalline appearance (more and more feebly in proportion as the degree of nitration is diminished) (Fig. 6) the corresponding films are amorphous or at least their X-ray diagrams indicate an amorphous structure (Fig. 7). The difference from this point of view between films of 12-95 per cent. N and those of 12 per cent. N is extremely clear (Figs. 1 and 7). In consequence it is necessary, in order to observe with certainty the changes in the lattice of nitrocellulose, to make use of compounds nitrated with an amount of nitrogen as near as possible to the maximum of nitration; this indicates that only trinitrocellulose is a well-defined compound, which can assume several forms, according to the solvent, when we pass from the disperse phase, whilst the presence of ill-defined compounds such as "dinitrocellulose" hinders this phenomenon and leads to films having an amorphous structure.

From analogous results obtained by Hess, Katz and Trogus on triacetylcelluloses precipitated from solution (and not evaporated in the form of films), and from results which we have ourselves obtained on films of trinitrocellulose, it follows that cellulosic compounds at the maximum degree of substitution are, just as natural cellulose, capable of assuming different crystalline forms when they pass from the stage of swelling followed by dispersion. Without doubt this will be of assistance in helping us to elucidate the structure of these complex bodies and in permitting us, in particular, to throw a light on the processes involved in swelling and dispersion, as well as on the nature of the forces which bind together the cellulosic chains.

# Changes of Structure of Nitrocellulosic Films in the Course of Drying.

We will now review rapidly the work we have carried out during the past year on the phenomena which take place during the drying of a film of nitrocellulose.

To this end we prepared collodions from nitrated cotton (C.P. I at 12.95 per cent.) by prolonged agitation with different solvents (acetone, ethyl acetate, amyl acetate, butyl acetate, etc.). The film was dried (whilst protected from moisture) at 70° C. for varying times; X-ray diagrams were taken at different periods of the drying, from fifteen minutes after flowing to 100 hours.



C. solvent, acetone. Fig. 2.—Dried 2 hrs. at  $70^{\circ}$  C. solvent, acetone. Fig. 1.-Dried 45 mins. at 70

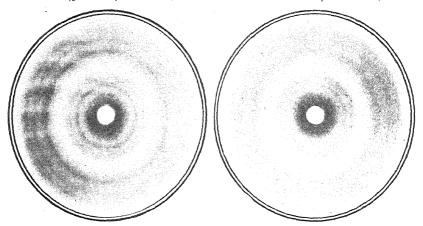


Fig. 3.—Dried 4-20 hrs. at 70° C. solvent, acetone. Fig. 4.—Dried 40 hrs. at 70° C. solvent, acetone.

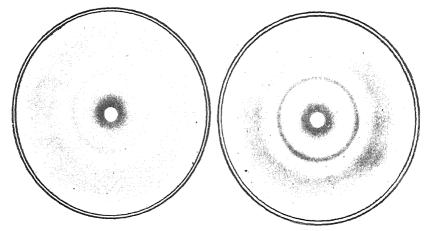
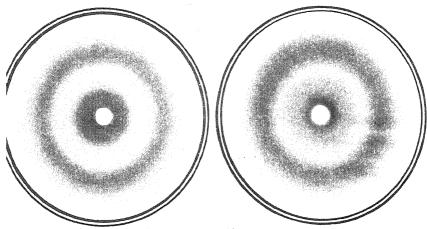
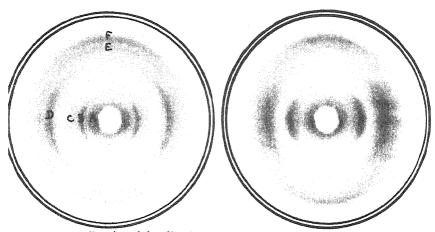


Fig. 5.—Dried 72 hrs. at 70° C. solvent, acetone. Fig. 6.—Cotton, nitrated to the extent of 12.95 per cent. N. (To fuce fage 80.



 $[ \mbox{Nitro-films, 12 per cent. $N$ solvent, acetone.} ] \\ \mbox{Fig. 7.—Dried 15 mins.} \\ \mbox{Fig. 8.—Dried 72 hrs.} \\$ 



Stretches of nitro-films (12'95 per cent. N solvent, acetone).

Fig. 9.—Dried 15 mins.

Fig. 10.—Dried 72 ltrs.

[See fuge 88.

In the case of films derived from acetone collodion, it is clear that the figures (1-6) show, according to the time of drying, important differences.

The diagram consists of a system of Debye-Scherrer rings indicating a very distinct crystalline structure, at any rate in the case of the films for which the period of drying did not exceed about forty hours. One series of these rings (that which corresponds to the small equidistances) is not sensibly modified in the course of the drying; other rings on the other hand (corresponding to the greater equidistances) are apparent at the beginning of drying but these disappear progressively.

Figs. I to 5 make it possible to follow these modifications; Table I.

summarises the results obtained.

TABLE I.

Time of	I	Exterior Rings.					
Drying.	А. В.		c.	, D.	E.	F.	
15 mins. 45 " 1½ hrs. 2 4 20 40 72 100	15·1Å. 15·1Å. 14·7 14·4 (?) Very weak disappeared ————————————————————————————————————	9.7Å. 9.5 9.4 9.3 9.3 9.3 9.3 9.3 disappeared	7-3Å. (?) 7-3 (?) 7-2 (?) 7-1 (?) 7-1 7-0 7-2 7-2 7-2	4·3Å. 4·4 4·5 4·6 4·6 4·6 (?) (?)	3.9Å. 3.9 3.9 3.9 3.9 3.9 (?)	3.5Å. 3.5 3.5 3.5 3.5 3.5 3.5 (?)	
Nitrated fibre C.P. 1 at 12.95 % N.	· <u>-</u>	<u></u>	7.0	4.7	4.0	3.4	

Note.—The sign (?) indicates that the ring is too weak or diffused to provide a satisfactory measurement.

Without entering into detail as to interpretation, since we are only here giving a résumé, it follows from the study of the diagrams that the films obtained from nitrocellulose of 12.9 per cent. N dissolved in acetone present a crystalline structure which changes during the course of drying, to finish up in the end as a structure similar to that of the nitrated cotton which served as a starting point (Fig. 6). This change consists essentially in the appearance of rings differing among themselves only in their greater equidistance, the other spacings remaining practically constant. The change once completed, *i.e.* the film being completely dried, we find again a diagram very similar to that of nitrated cotton; it is only during the period when the film still contains solvent that these discontinuous modifications of the lattice are evident.

Analogous results are obtained when ethyl acetate is used as solvent. But though the phenomena are comparable the absolute value of the periods of identity which appear at the beginning of the drying are not the same. Here also the variations in the lattice of the nitrocellulose are found principally only in the greater equidistances.

When using butyl or amyl acetate, on the other hand, these phenomena become less clear and even almost completely disappear; we obtain then immediately a diagram similar to that of Fig. 5 or Fig. 6, corresponding to the ordinary lattice of trinitrocellulose without modi-

fication. It should be noted that these substances are already poor solvents. It is the same with 50 per cent. mixtures of butyl or amyl acetate with acetone.

These results have been verified with cotton nitrated to 13.8 per cent. N (very nearly trinitrocellulose) as well as with collodions of different concentrations. It is interesting to note on the other hand that with films made from 12 per cent. N nitrocellulose the diagrams obtained are no longer composed of crystalline rings but of amorphous haloes; an explanation has been given above. In this case, nevertheless, we can also observe modifications in the diagrams during the course of the drying, but these changes are naturally less clear than when we are dealing with Debye-Scherrer rings (Figs. 7 and 8).

Finally, we would also remark that it is possible to obtain the same phenomena when drying the films at ordinary temperature (18° C.) when the drying is carried out *in dry air*. In this case the change and the modifications in the lattice obviously take place more slowly than

at a temperature of 70° C.

### Interpretation of Results.

As a result of this work, as well as of that which we have carried out on celluloid, we are led to believe that these modifications of the lattice of trinitrocellulose are in reality modifications resulting from the presence of the solvent and due to an addition compound. The hypothesis of a solid solution would appear in effect to have to be excluded. The mechanism can be attributed to successive contractions following one direction, of the lattice originally swollen with solvent; these discontinuous contractions accompany the departure of the solvent, each of the crystalline forms disappearing progressively to give place to the next.

With the object of further investigating the manner in which these changes in the lattice of trinitrocellulose are brought about, we made a series of diagrams whilst stretching the films at different stages of the drying. The figures obtained thus give evidence of orientation phenomena (Faserdiagram) (Figs. 9 and 10). In particular we notice that the rings ABC, characterising the different stages of drying, are caused by interferences on planes passing approximately through the direction of the stretching; the same thing shows in the plane D. On the other hand, the exterior rings E and F, which show only intensification in the polar direction, are in planes approximately perpendicular to the direction of stretching. In consequence the changes in the lattice which are indicated by the appearance of the rings A and B arise from an increase in the spacings of planes which are approximately parallel to the axis of the fibre; if we admit that this axis coincides with the direction of the principal valency bonds, we arrive at the conclusion that the links of the lattice of trinitrocellulose distend or collapse perpendicularly to the direction of the glucoside chains.

According to the theory of Meyer and Mark it is exactly in this direction that we find the linkage forces most feeble, the chains being kept together only by secondary valencies, whilst the glucoside groupings are bound by primary valencies. We can understand then how it is that the action of the solvent tends to manifest itself by the separation of chains much more than by their breaking and that the lattice can vary more readily in this direction than in the other, since this variation

corresponds to a smaller display of energy.

This result accords with the swelling of a fibre, which is accompanied by an enlargement of the lattice due to an intramicellar action of the solvent; in the present case we are concerned with the opposite phenomenon or "collapse."

To sum up: our results show that nitrocellulose in the neighbourhood of the maximum of nitration is capable of taking on different crystalline forms by combining with certain swelling media. X-ray spectrography makes it possible to see these changes and to follow, notably, the phenomena due to drying, to ageing, as well as to the influence of different solvents, certain of which have a specific action on nitrocellulose.

It is probable also that the differences in the mechanical properties between films made from nitrated cotton in which the degree of nitration is equal to 12.95 per cent. and those in which the degree equals 10 per cent. or 12 per cent., are due in large measure to the fact that, in the first case, the films have an accentuated crystalline structure, whilst they are amorphous in the second case. Other very recent experiments, based on electronic diffraction (Kirchner, Taylor Jones, Dauvillier), have also shown that films of pure nitrocellulose sometimes give beautiful interference effects due to single crystals. So far it has not been possible to give a complete interpretation of these diagrams; but one essential fact follows nevertheless, namely, that they demonstrate the presence of crystals. From this point of view electronic diffraction seems to provide a method of great interest, and we propose to utilise the apparatus which we have constructed in the laboratory of Mr. M. de Broglie 3 with the object of ascertaining precisely the conditions under which these interference phenomena appear.

The studies which are the object of this short memoir are being continued in the research laboratory of the Société Kodak Pathé in Paris, whom we desire to thank here for the assistance and interest which have so kindly been afforded to us.

<sup>3</sup> J. J. Trillat and Th. v. Hirsch, Z. Physik, 75B, H. 11, 1932; and J. Physique, May, 1932.

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# SURFACE FILMS OF CELLULOSE DERIVATIVES ON AQUEOUS SOLUTIONS.

By N. K. Adam.

(Received 24th May, 1932.)

This paper records the results of measurements of the surface pressure and area of extremely thin films of cellulose derivatives, spread on carefully cleaned surfaces of water or aqueous solutions. The surface pressure is the outward force which a spread surface film exerts on a barrier dividing the film-covered surface from a clean surface. The work was undertaken in the hope of gaining information about the mechanical properties of the cellulose molecules, and their adhesional fields of force, since a great deal of information has been obtained in a similar way about the molecules of long chain aliphatic compounds.

Previous studies of films of cellulose derivatives on water have been published by Katz and Samwel, Zocher and Stiebel, and Davey and de Vore; a comparison of their results with mine, and a discussion

of their meaning will be given in the course of this paper.

The state of the surface films has also been examined by the ultramicroscopic method of Zocher and Stiebel, in which a cardioid condenser fitted in the bottom of the trough is focussed on the surface. The cellulose derivatives often do not spread completely, but are partly precipitated on the surface, and this method is invaluable in detecting incomplete spreading. I am indebted to Professor Katz for calling my attention to its importance; it had not been introduced at the time when his work on spreading cellulose derivatives was done.

#### Experimental Technique.

The surface pressure was measured by the method introduced by Adam and Jessop in 1926, 4 as a modification of Langmuir's technique. The water is contained in a brass trough filled to the brim, the cleaning of the surface and manipulation of the films being accomplished by paraffined glass strips laid across the trough. The floating barrier dividing the film from a clean surface is connected to the side by very thin and flexible platinum ribbons, which prevent the film passing, while allowing enough freedom of motion to allow the surface pressure to be measured to 0.02 dynes per centimetre. A system of torsion wires measures the outward force or surface pressure of the film. The details of the trough and instrument, slightly modified from the 1926 instrument, were exactly as described in my book. 5 Two instruments were used, of different sensitivity, one for pressures from 0.02 to about 3 dynes per centimetre, and the other for pressures above 0.5 dynes.

The areas of the films (expressed in sq. Å. per hexose group) were measured by dropping known amounts of the cellulose derivatives,

<sup>&</sup>lt;sup>1</sup> Annalen, 472, 241, 1929. <sup>2</sup> Z. physikal. Chem., 147 A, 401, 1930.

<sup>&</sup>lt;sup>3</sup> J. Physical Chemistry, 35, 2129, 1931.

<sup>&</sup>lt;sup>4</sup> Proc. Roy. Soc., 110 A, 423, 1926.
<sup>5</sup> The Physics and Chemistry of Surfaces, pp. 35 to 42, Clarendon Press, 1930.

dissolved in carefully purified organic solvents, on to the surface, using a calibrated dropping pipette. The length of the film was measured with a scale.

The ultramicroscopic examination was conducted in nearly the same way as that described by Zocher and Stiebel, with minor modifications. A cardioid condenser (by Zeiss) was inserted with sliding fit into a standard sleeve fixed in the bottom of the trough. The microscope was an inexpensive vertical stand, with the stage removed; it was placed on the table with the tube overhanging the trough and moved until the objective was centrally over the cardioid. A Zeiss spotlight was used as source of illumination. The cardioid requires to be very accurately focussed on the surface. This was effected as follows: a quantity of a nitrocellulose previously found to spread imperfectly was placed on the surface, the cardioid was then roughly focussed by sliding in the sleeve by hand, and the final adjustment of focus was made by sucking up more or less liquid out of the trough into a 100 c.c. pipette fixed vertically at one end of the trough. Very accurate adjustment of the level of the liquid, and consequently of the focus, could be attained in this way, and the necessity of a complicated substage focussing arrangement was avoided. A low power of the microscope (objective  $\frac{2}{3}$  or  $\frac{1}{2}$ ) was found most convenient. The ultramicroscopic examination could be conducted simultaneously with the measurement of surface pressure, the pressure measuring instrument being fixed at one end of the trough and the cardioid near the middle. In order to clean the surface the microscope tube was simply racked up about half an inch to allow the barriers to pass underneath; this did not disturb the focussing of the cardioid, and the microscope was easily refocussed on the surface after cleaning.

This method has the disadvantage that one end of the film is fixed by the surface pressure instrument, so that only a small part of the surface can be examined without altering the area and the surface pressure considerably. If examination of a larger area seemed desirable, the pressure measuring instrument was removed and the film was moved along the trough between two glass strips linked together so as to keep the area constant. In this way a strip extending the whole length of the film could be examined; and often, by gentle blowing, other parts of the surface could be brought into the field.

#### Materials.

Numerous specimens of cellulose nitrates were received from Imperial Chemical Industries, Ltd., Ardeer, the range of nitrogen content being from 10·9 to 13·9 per cent. nitrogen. The viscosities ranged from 0·00458 to 0·0496 c.g.s. units at 20° in 0·5 per cent. solution in 99·8 per cent. acetone. Professor K. Hess of Berlin also kindly sent me several specimens ranging from 12·2 to 13·5 per cent. nitrogen, of a wide range of viscosities. The fibrous structure of the original cellulose was scarcely impaired in some of the specimens; in others it was completely destroyed to the eye.

The esters with fatty acids included numerous specimens of the acetates (from Professor Hess, Mr. D. J. Bell, and Imperial Chemical Industries, Ltd.); one specimen of the tripropionate from Professor Hess; a butyrate containing about 2½ butyryl groups per hexose from Imperial Chemical Industries, Ltd.; and specimens of the laurate,

palmitate, and stearate from the above sources and from Professor Karrer of Zurich.

The ethers included benzyl ethers (2.0 to 2.66 benzyl groups per hexose) from Imperial Chemical Industries, Ltd.; methyl ethers, both fibrous and crystalline, from Professor Hess and Mr. Bell; and crystalline triethyl cellulose from Professor Hess. Professor Haworth also kindly sent some trimethyl amylose, and several fully methylated disaccharides of known constitution were received from Professor Haworth and Mr. Bell. I am most deeply indebted to all these colleagues for their gifts of specimens, without which the work could not have been done.

#### Results.

#### Benzyl Ethers.

The benzyl ethers spread completely on water, from a solution in benzene 5, alcohol 2 parts by volume; no sign of collapse was found

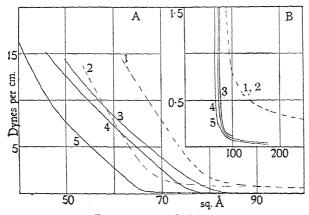


Fig. 1.-Benzyl Cellulose.

- 1. 2.66 on 2N NaOH.
- 2. 2.0 on NaOH.
- 3. 2.66 benzyl groups. 4. 2.37 benzyl groups. 5. 2.0 benzyl groups.

with the ultramicroscope, films being optically empty except for accidental particles of dust, which are very easily distinguished the colfilms. lapsed Five specimens were examined, three containing 2.0 benzyl groups per hexose, one 2.37, and one 2.66 groups. The area of the film increasessomewhat with increasing number of benzyl

groups, but otherwise the surface pressure-area curves (Fig. 1) are very similar. The inset curve shows the continuation of the main curves to greater areas and lower pressures, on a different scale. In all cases the surface pressure has fallen to less than 0.1 dyne at 100 sq. A. per hexose, and less than 0.05 dyne at 150 sq. Å. The main portion of curves 3, 4, 5 indicates an area per hexose group, extrapolated to no compression, of about 66 sq. A. for the dibenzyl cellulose; 78 for 2.37 benzyl groups, and 82 for 2.66 groups. The curves are beautifully reversible without hysteresis, except below 0.5 dyne per centimetre, where there is a slight tendency for the pressures to be higher for a minute or two after putting on the film than later. The films, tested with talc sprinkled on the surface, were decidedly viscous, but were not solid below 20 dynes pressures. Change of temperature from 13° to 83° had no appreciable effect on the form of the curves above 0.5 dynes; the effect of temperature at lower pressures could not be accurately examined on account of convection currents.

On twice normal caustic soda solution, the dotted curves I and 2 were obtained for  $2\cdot0$  and  $2\cdot66$  benzyl groups. They lie somewhat to the right of the curves on water, though a part of this difference may be due to accidental contamination of the surface, which is impossible to eliminate completely with soda solutions. The most important difference is found at pressures below one dyne; the curve does not tend to a definite area per molecule but becomes asymptotic to the abscissa. This tendency to approach the axis of no pressure very gradually is general with the celluloses on soda, and is probably not wholly due to accidental contamination.

### Methyl and Ethyl Ethers.

These also spread completely on water from chloroform solution, giving optically empty films. They differ from the films of benzyl ethers in one important respect; even on water the curves do not tend to a definite area at low compressions, but approach the line of no pressure asymptotically (Fig. 2). At 100 sq. Å. the pressures are 0.7 dyne or

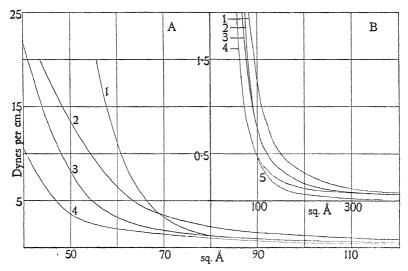


Fig. 2.—Methyl and Ethyl Celluloses.

- I. Triethyl cellulose (cryst.).
- Trimethyl cellulose (cryst.).
   Trimethyl cellulose (fibrous).
- 4. Diacetyl monomethyl cellulose and trimethyl amylose (incompletely spread).
- r. Trimethyl (cryst.).
- 2. Triethyl (cryst.).
  3. Trimethyl (fibrous).
- 4. Diacetyl monomethyl.5. Trimethyl amylose.

more, and easily measurable pressures are obtained up to 400 sq. Å. The largest areas in this group were given by Hess' crystalline trimethyl cellulose; <sup>6</sup> slightly smaller areas, though very similar curves, were obtained with trimethyl ramie, <sup>7</sup> in which the fibrous structure was present and even the lustre of the original ramie was not very much diminished. Bell's trimethyl cellulose, recovered from chloroform solution, gave exactly the same result as the trimethyl ramie; and another of his specimens, obtained by acetylation followed by drastic methylation

<sup>6</sup> Annalen, 450, 29, 1926.

<sup>&</sup>lt;sup>7</sup> Z. physikal. Chem., 4 B, 322, 1929.

with methyl sulphate and alkali, repeated five times, which was believed to have undergone some de-polymerisation, gave the same result as Hess' crystalline material. It appears therefore that the more highly degraded methyl celluloses spread to slightly greater areas than those with longer chains. Temperature had practically no influence on the form of the curves.

On 2N caustic soda the curves (not reproduced here) had the same shape but slightly greater areas, the difference being probably just

outside the error due to the additional contamination.

Triethyl cellulose (crystalline, Hess) <sup>8</sup> gave a curve coincident at low pressures with that for the fibrous trimethyl cellulose, but at higher pressures decidedly larger areas were obtained. This is no doubt due to the larger size of the ethyl groups.

The areas for methyl and ethyl cellulose at medium and high pressures are some 10 per cent. greater than those recorded by Katz and Samwel, an unimportant difference. The gradual, asymptotic approach of the curves to axis of no pressure is a new observation, but Katz and Samwel used the earlier form of Langmuir's instrument, in which the measurement of low pressures is rendered very difficult by the air jets necessary to prevent leaks past the floating barrier. They did not record pressures

below about 2 dynes, so there is no discrepancy.

A cellulose derivative having approximately the composition of a di-acetyl monomethyl cellulose (Bell) spread not quite completely, but at low pressures the curve of apparent areas was asymptotic, like the methylated celluloses. It occupies an intermediate position between the tri-acetyl celluloses, which spread incompletely and show no asymptotic trend (see below), and the pure methyl and ethyl ethers, which give asymptotic curves and spread completely.

Haworth's "trimethyl amylose," a derivative of starch, not cellulose, was not quite completely spread. It approached the line of no pressure somewhat gradually, yet the pressures are never so great, at equal (estimated) areas, as those of the methylated celluloses, in the low pressure region. Above 100 sq. A., the pressure falls off much more rapidly than any of the others. From the position of the curve at higher pressures, it was estimated that 80 to 90 per cent. of the material was spread, assuming a curve for the fully spread material resembling that of the cellulose derivatives. At 350 sq. A. the pressure was less than 0.02 dynes per centimetre, decidedly lower than with the trimethyl celluloses. It would require further investigation to establish whether methylated starch derivatives spread less completely, in general, than methylated celluloses; but it is noteworthy that all the methylated celluloses tried spread completely, and the single specimen of a methylated starch does not. Perhaps this is due to the stereochemistry of the molecule rendering it more difficult to uncoil the starch chain completely and flat, than the cellulose chain.

In order to examine the effect of chain length on the properties of the spread films further, an attempt was made to spread three specimens of fully methylated bioses, namely heptamethyl  $\beta$ -methyl lactoside, heptamethyl  $\beta$ -methyl cellobioside (from Mr. Bell), and heptamethyl  $\beta$ -methyl gentiobioside (from Professor Haworth). Unfortunately these substances all dissolved too readily to form films.

#### Cellulose Nitrates.

On water, aqueous acetone, and dilute hydrochloric acid, nitrocelluloses never spread to more than a slight extent, unspread aggregates of very various shapes and dimensions being always visible under the cardioid ultramicroscopic illumination, and occasionally even to the naked eye. The aggregates are separated by fair-sized dark patches. which probably consist of fully spread, monomolecular film. The surface will sustain a fair compression without rapid collapse at small areas, indicating that, once spread, the nitrocellulose film is fairly stable on water. The apparent areas, which are a measure of the fraction of the material spread, vary somewhat with the solvent used for the nitrocellulose; ethyl acetate often gives larger apparent areas than butyl acetate. The apparent areas do not vary much with temperature, and are fairly reproducible with a given solution; they vary from 10 sq. Å. or less per hexose up to 30, at low compression. The film being obviously heterogeneous, the apparent areas are useless for determining the size of the nitrocellulose particles.\* Ethyl acetate, star solvent (ethyl acetate and alcohol), butyl acetate, methyl cyclohexanone, and benzeneacetone (5:2 by volume) were tried as solvents. As a rule, the nitrocelluloses with less than 12.6 per cent. nitrogen spread more than the high nitrogen specimens. There was little, if any, more spreading from less volatile solvents than from the most volatile.

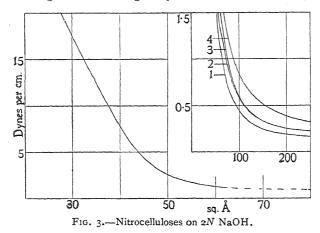
In the hope of increasing the attraction between the cellulose nitrates and the water, various aqueous solutions which might be expected to act chemically on the nitrate groups, were tried. On sodium stannite, containing 2N caustic soda and M/20 stannous chloride, also M/4 sodium sulphide, and 0.9M ferrous sulphate, the nitrocelluloses did not spread completely. Molar sodium sulphide gave a solution so dirty that its surface could not be cleaned sufficiently to allow of film work.

Sodium hydroxide, however, 2N strength,† gave films, apparently fully spread, of all the nitrocelluloses containing less than 12·6 per cent. nitrogen, from solutions in ethyl acetate, butyl acetate, and methyl cyclohexanone. The surface pressure-area relation was practically the same for all these solvents, and was independent of nitrogen content (provided this was less than 12·6 per cent.) and independent of viscosity, above 2 dynes per centimetre. The curves are shown in Fig. 3. At very low pressures (inset curve) there appears to be a slight difference

+ Variation of the strength of soda from 1.64 to 2.36N made little difference to the results. Dilute soda (N/10) had no more spreading power than water.

<sup>\*</sup> Davey and de Vore <sup>3</sup> found that the apparent area to which nitrocellulose, solutions spread on water increases with increasing dilution of the solution using ethyl acetate as solvent. They conclude that the size of the micelle of nitrocellulose in the solution decreases with increasing dilution. This, however, assumes that the spreading consists simply in rearranging the micelles present in the solution, without change, in a layer one micelle thick on the surface of the water, closely packed; this assumption is obviously incorrect in the light of the ultramicroscopic examination, which was not employed by these authors. The surface is extremely heterogeneous, whereas a uniform layer of close-packed micelles would be homogeneous, if not optically empty. There is little doubt that, as the solution spreads on the water surface, a large part of the material is precipitated by the action of the non-solvent water, only a part being spread to a uniform film; and this spread part is probably one molecule, or rather one hexose group, thick, like the fully spread cellulose derivatives. Since the surface is not homogeneous, the apparent areas are no guide to the size of the precipitated particles; and it is improbable that even if these precipitated particles were uniform in size (which they certainly are not, on inspection), they would be similar in size to the particles in solution.

between the specimens of different viscosity, those of lower viscosity showing somewhat higher pressures. The viscosity of the specimens



I, 2, 3, 4 determined in 0.5 per cent. solution in 99.8 per cent. acetone at 20°. were 0.0496, 0.0151, 0.00542, 0.00458 and c.g.s. units respectively. The experimental error involved in the measurement of pressure on those strong caustic soda solutions, at low pressures, is so

great that no stress can be laid on these differences; the probable error is at least o·I dyne per centimetre. Ethyl acetate was the solvent used in these low pressure determinations; the less volatile butyl acetate and methyl cyclohexanone left residues on the surface long enough to make measurements of pressures below one dyne practically impossible on the easily contaminated soda solutions.

Benzene-acetone (5:2 by volume) failed to spread any nitrocellulose completely on soda, the precipitated fraction being present, however, in the form of much finer aggregates than in the case of nitrocellulose spread on water. The apparent areas (i.e., the fraction spread) had no obvious relation either to nitrogen content or to viscosity, from this solution.

It is noteworthy that, on caustic soda, the curves always become asymptotic to the axis of no pressure; on water, however, the curves (not reproduced here) of the pressure of the partially spread film at various apparent areas always fall to a few hundredths of a dyne at areas only slightly greater than those at which several dynes are shown. Some part of the asymptotic tendency may be ascribed to the natural contamination always existing on caustic soda solutions, but a part of the effect is believed to be genuine. All the cellulose derivatives tend to spread to considerable areas, below I dyne, on 2N soda. Only the methyl and ethyl ethers do so on water.

An attempt was made to decide how rapidly the nitrate groups are hydrolysed off the nitrocellulose after the films are spread on soda. The film was spread, and allowed to remain for a known time; it was then suddenly compressed between barriers to a very small area, so that the greater part of the material was squeezed out of the film; and by means of a bent thin glass rod, some of the crumpled film was swept up and removed on to a microscope slide. Addition of diphenylamine in sulphuric acid gave a blue colour with material which had not been spread more than about a minute, showing that the nitrate groups had not been completely hydrolysed off in this time; after longer periods in the spread film the strong soda had removed the nitrate so completely that the diphenylamine test could not be obtained.

The results of the surface pressure measurements must therefore be interpreted as applying to largely hydrolysed material, most, but probably not all, of the nitrate groups having been removed.

### Alkyl Nitrates.

In order to estimate the degree of adhesion of the nitric ester endgroup for water, which is one of the important factors in determining the spreading of nitrocellulose, it was thought desirable to compare the spreading of long chain alkyl nitrates with long chain compounds containing other end-groups. Specimens of hexadecyl and dodecyl nitrates were therefore prepared by Bouveault and Wahl's method,<sup>9</sup> stirring the pure alcohol with excess of the strongest nitric acid obtainable by distilling ordinary fuming acid with sulphuric acid under somewhat reduced pressure, extracting with ether, washing and drying in vacuo.

The preparations were not pure (m.p.'s, dodecyl, mostly liquid at 0°; hexadecyl, one specimen, ca. 4-10°; another specimen, ca. 7-10° with a small amount of white solid remaining up to nearly 20°). Analyses (for which I am indebted to Imperial Chemical Industries, Ltd., Ardeer) showed about 12 per cent. deficiency of nitrogen in the dodecyl nitrate (found, 5·22, 5·40 per cent., theory 6·06); about 8·5 per cent. deficiency in one specimen of hexadecyl nitrate (4·46, 4·49 per cent, theory 4·89); about 22·5 per cent. excess in the other hexadecyl nitrate (5·95, 6·01 per cent.). The deficiency is likely to be due to fatty acid formed by oxidation, or to unchanged alcohol; the excess of nitrogen is more difficult to account for, unless a small amount of nitration of the hydrocarbon chain had occurred.

Spreading on water was very incomplete. Hexadecyl nitrate (both specimens) gave no surface pressure above 40 sq. Å.; between 40 and 30 sq. Å. a very unstable, collapsing film, probably of the liquid expanded type, which could not withstand a pressure of 4 dynes per centimetre. The ultramicroscope showed a "punktstruktur" (numerous fine points of orange coloured light) like that described by Zocher and Stiebel.<sup>2</sup> With dodecyl nitrate no surface pressure could be obtained at any areas.

Further purification of the nitrates was not attempted, in view of the difficulty of distilling or re-crystallising them, and the fact that the spreading was so poor. The likely impurities (fatty acid or alcohol) both spread well; hence the spreading power of pure nitrates would probably have been less than that of the specimens used. Clearly the adhesion of the nitrate group for water is insufficient to give a stable film. The acetates of long chain alcohols give stable films; 10 hence the nitrate group has less adhesion for water than the acetate. To confirm this, a rough comparison of the solubilities of ethyl nitrate and acetate in water was made, showing that ethyl acetate is from seven to nine times as soluble as ethyl nitrate. The stability of hexadecyl nitrate in the films is roughly the same as that of hexadecyl methyl ether; 11 hence the nitrate group has (very roughly) the same anchoring power to water as a methoxyl group.

Bull. Soc. Chim., Paris, (3), 29, 957, 1903.
 Adam and Dyer, Proc. Roy. Soc., 106 A, 697, 1924.
 Ibid., 698, 1924.

#### Cellulose Acetates.

The acetates ranged in composition from approximately the diacetate to the triacetate, and included crystalline and fibrous specimens. In no case was spreading complete on water, though probably upwards of 70 per cent. of the material often spread to a monomolecular film. The ultramicroscope showed a small amount of unspread material in all cases. The left-hand curve in Fig. 4 shows the results obtained with both Hess' crystalline and fibrous triacetyl cellulose. It agrees well with those of Katz and Samwel's curves on acetates which show the largest areas. The pressure was below 0·1 dynes at 75 sq. Å., and below 0·025 at 150 sq. Å.

On 2N soda the curves for these two triacetyl celluloses at low pressures become asymptotic to the axis, being practically the same as curve I in Fig. 3 for the nitrocelluloses. The material is apparently fully spread. These films will not, however, stand much compression; at 4 or 5 dynes per centimetre, the film collapses. It is curiously difficult to find ultramicroscopic aggregates during this collapse, yet from the behaviour of the surface pressure, which could not be forced above 5 or 6 dynes, with constantly and rapidly diminishing area, there can be

little doubt that the film is actually collapsing.

None of the other triacetates or lower acetylated celluloses tried gave larger areas than these, and some seemed to be even less spread. In view of the incomplete spreading on water, and the ready collapse under pressure on soda, the acetates were not further studied; it is clear from the curve that the acetate films, once spread, are generally similar to the films of the other derivatives, which do not show the

asymptotic approach to the line of no pressure.

Zocher and Stiebel <sup>12</sup> reported that cellulose acetate films on water are optically empty, as if they were fully spread, which disagrees with my observations. They record, however, "thicknesses" of the spread films which agree fairly well with the areas obtained by Katz and Samwel and myself, so that it seems probable that their acetates behaved on spreading in much the same way as ours. A possible reason for this discrepancy is that (according to my observations) the unspread patches of acetate are generally very local; the greater part of the surface, I agree, is optically empty, but if the whole length of the film is examined by moving the film over the cardioid by a pair of barriers fixed a constant distance apart, unspread regions of greater or less extent have always been found. It is possible that their observations were confined to one small area of the film, which happened to be optically empty.

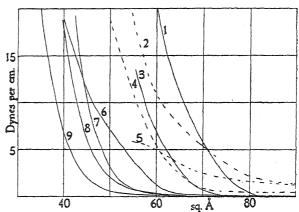
#### Esters of Higher Fatty Acids.

Curves for esters with various acids from propionic to stearic are also given in Fig. 4. None of the esters spread quite completely according to ultramicroscopic observations, yet from the areas one must conclude that the greater part was spread. The lower esters were spread from chloroform solution, the laurates to stearates from benzene. On water, there is no asymptotic approach to the line of no pressure; on 2N soda there is, and the areas are much greater. The films of stearate could not be successfully examined on soda, as they continually expanded in area. This is rationally explained by slow hydrolysis of the ester,

setting free stearic acid, which is known to form a gaseous film on 2N soda.

Since the films were not fully spread, the information which can be derived from the areas is scanty. Even with the longest chain esters

(stearates), the area is greater than that of the same number of hydrocarbon chains packed closely and upright, as in the condensed film of long chain If compounds. the films were fully spread, and chains the in the stearates were closely packed and would be about 41 for the distearate and 61 for the tristearate, and would



vertical, the area Fig. 4.-Fatty acid esters of cellulose (not fully spread on water).

- 1. Tristearate.
- 2. Tripropionate on NaOH.
- 3. Dilaurate.
  4. 2½ butyrate on NaOH.
- 5. Triacetate on NaOH.
- 6. 2½ butyrate.
- 7. Distearate.8. Tripropionate.
- 9. Triacetate.

vary very little with pressure. Actually the apparent areas, which must be less than the real areas in the film, are considerably greater than this at low compressions, and there is considerable compressibility.

It must be concluded that the hexose ring, lying flat on the surface in the films, occupies an area greater than the three eighteen carbon chains; and that lateral compression of the film allows some re-arrangement of the hexose rings next the water, which form the base of the film, the superstructure of which no doubt consists of the long chains arranged at a fairly steep angle to the surface. The lateral adhesion between the long 18 carbon chains is not sufficient to counteract the tendency of the hexose rings to lie flat.

My apparent areas for the tripropionate are somewhat greater, and for the tristearate somewhat smaller, than those of Katz and Samwel; the difference is unimportant, especially as the materials are not quite fully spread; the general form of the curves is the same.

#### Cellulose.

A cuprammonium solution of cellulose was practically completely precipitated, not spread, on water.

#### Temperature.

In no case did change of temperature seriously affect the form of the curves. This was frequently tried over the range 15° to 50°; in one case up to 84°.

#### Discussion.

#### (a) Structure of the Fully Spread Films.

There is little doubt that the cellulose chains lie flat in the water, at least at low compressions, with every hexose group in contact with the water. The area is of the right order of magnitude for this; the curves give the area as 55 to 60 sq. Å. for each hexose group at about 2 dynes per centimetre, except in the benzyl ethers, where it is somewhat larger. If a model is made up, according to the usually accepted formula of cellulose and placed on the table with every glucose ring flat, the area

covered by each, with all hydrogen and oxygen atoms included, is about 52 sq. Å., the width being about 10 Å. and the length of each (a quantity determined exactly by X-ray studies) 5.15 Å. The area occupied by the esters and ethers should be rather larger than this. Too much reliance should not be placed on areas estimated in this way, as although the models of individual molecules can be made fairly accurate, the closeness with which they are packed side by side in Nature is an uncertain factor. It is clear, however, that there is sufficient room in the films for the chains to lie with all the hexose rings flat on the water.

The curves show considerable compressibility in the films, which indicates changes in either orientation or packing of the molecules, or both, as the lateral compression is varied. It seems certain that these changes are caused by the chains bending. According to the formula for cellulose, there should be two joints at the junction between successive hexose rings in the chains, owing to possible rotation about the carbon to oxygen bonds, and the presence of these joints renders the long chain fairly flexible in the models.

Compression of the models, allowing the chains to bend, can alter the area slightly, without removing the rings from the plane of the water; there is much more possibility of diminution of area if the rings are somewhat tilted on compressing laterally. It is unlikely, however, that the rings will be tilted very far from the water, without causing collapse of the film; for there are so many water attracting groups in each ring, that the stable anchorage of the film to the water probably depends on every ring being fairly close to the surface. The films could be compressed and re-expanded almost reversibly, without appreciable hysteresis.

Another way in which flexibility of the chains may operate to cause areas greater than the minimum to which the chains could pack closely, is through vibration of the chains, spontaneous flexure and whipping about occurring throughout their length. If the thermal agitation of the chains is sufficient to overcome to some extent the lateral adhesive forces which cause the chains to lie side by side in the fibre, and cause these vibrations, the area in the spread films may increase to almost any amount. Haller <sup>13</sup> has suggested a theory of the osmotic pressure of organic colloids, in which such a vibratory motion is taken into account, in addition to the translational kinetic energy of the molecules, which will certainly be small in the case of these extremely large molecules. With long chains, and fairly small volumes (in three dimensions) or small areas (in two dimensions), the contribution to the outward pressure on a membrane impermeable to the dissolved substance may be very much greater than that due to translational motion.

The float of the surface pressure measuring apparatus is a most perfect semipermeable membrane, as it completely prevents the insoluble and non-volatile film passing, and allows water to pass under the float with perfect freedom; as has been frequently pointed out before, the surface pressure is a two-dimensional osmotic pressure. In the case of these colloidal substances, we may call the surface pressure a two-dimensional "swelling pressure," at least at small and medium areas. There is no difference in principle between swelling and osmotic pressures, the former being the more appropriate term for mixtures very strong in colloid, the latter for dilute mixtures.

It seems likely that the "asymptotic" trend of some of the curves, approaching the line of no pressure very gradually, is due to extensive whipping and vibration of the chains, in the plane of the surface. In those films which show this asymptotic trend, the lateral adhesion between the chains is probably insufficient to restrain the thermal motions, so that when the lateral compression is low, the films expand to considerable areas. Of course the tendency of the chains to separate will be much greater in the spread films on water than in the dry cellulose derivatives, for the motions of the water molecules underlying the film will always have a disrupting action, antagonising the adhesive forces between the chains. If this explanation is correct, it must be concluded that there is less lateral adhesion between the chains spread on water, in the case of the methyl and ethyl ethers, than with any of the other substances, and that the lateral adhesion on 2N soda is less than that on water with all the cellulose derivatives.

#### (b) Size of the Different Derivatives.

There is no very marked difference between the films of different derivatives. The nitrocelluloses have, at moderate pressures, the smallest areas; and the benzyl celluloses show a definite increase in area as the proportion of bulky benzyl groups is increased. This is not surprising, as benzyl must be a large group. The differences between the other derivatives are complicated by the possible presence of the vibratory motions, which mask the size of the groups (the area which they would occupy if practically stationary), and it is difficult to say which of the derivatives has the larger area.

The viscosity of the specimens has no effect (except one so small as to be doubtful, with the nitrocelluloses on soda at very low pressures) on the area of the films; this was also noticed by Katz and Samwel. Increasing viscosity probably means longer chains; the length of the chains should not make a measurable difference to the space required by the hexose units, since the chains are probably spread out with the groups lying flat on the surface.

 $<sup>^{13}\</sup> Kolloid\text{-}Z.,$  49, 74, 1929. I am indebted to Mr. F. D. Miles for calling my attention to this theory and its possible application to the spread films.

## (c) Adhesional Forces.

The films spread to a layer one hexose group in thickness, probably in all cases; where the spreading is incomplete, it seems likely that the spread portion is one hexose group thick, the rest being heaped up in aggregates of very much greater thickness, which are visible in the ultramicroscope. As Katz and Samwel pointed out, this shows that the solutions contain no micelles, or bundles of parallel adhering chains, stable enough to resist disruption by the spreading forces of the water. There is probably some tendency of the chains to aggregate, for the work of Stewart and others has shown that swarms of molecules, more or less definite, generally exist in liquids with much the same packing as that adopted in the solid state, and these cellulose chains have a particularly strong tendency to aggregate side by side in the solid. But such micelles, if they exist at all in the solution, are evidently very unstable structures.

The differences between the derivatives in ease of spreading cannot be wholly explained by differences in the attractive power of the oxygenated groups for water. Thus the ethers spread much better than any of the esters; yet, from studies of long chain fatty compounds,14 it is found that ether groups have a much smaller adhesion for water than such ester groups as the acetate, and have an adhesion similar to that of the nitrate group. The extent of spreading depends on the relative intensity of two oppositely acting adhesions; that of the cellulose derivatives for the water, and the self-adhesion of the cellulose. When the solution is dropped on water, the water may precipitate the celluloses in bulk, or the chains may separate from each other and spread out to a uniform sheet; the amount of spreading depends on the relative rates of these two processes, as the solvent dries off. Since the ethers spread better than the esters, although the adhesion to water is not greater than that of the ester groups, there must be a stronger tendency of the cellulose ester chains to adhere laterally, than of the cellulose ether chains. The differences in spreading of the various specimens of nitrocellulose can be explained on the basis of the adhesion to water; there is incomplete spreading, even on soda, if the nitrogen content exceeds 12.6 per cent., i.e., if there is less than one free hydroxyl group per two glucose rings. This is no doubt due to the hydroxy! having a much greater adhesion to water than the nitrate groups.

Cellulose itself could not be spread, yet the adhesion of hydroxyl groups for water is high. This shows that the lateral adhesive forces, between chains of cellulose, must be much larger than the adhesion between chains of any of the derivatives here studied. This exceptionally high lateral adhesion is probably the cause also of the insolubility of cellulose.

(d) The incomplete spreading of the trimethyl amylose, a starch derivative, raises a very interesting stereochemical point. All the fully methylated celluloses spread completely; there is not likely to be much difference between the adhesion of the methyl ether groups in starch and in cellulose, since each is composed of the same glucose units. But if the models are made up according to the formulæ given by Haworth, the cellulose chain is found to lie out quite flat, without distortion, in a straight line, but the starch model, composed of maltose groups.

Adam and Dyer, Proc. Roy. Soc., 106 A, 698, 1924.
 The Constitution of Sugars, p. 84, 1929.

refuses to lie flat or straight. This may be the cause of the poor spreading of methylated starch, as opposed to methylated cellulose; Haworth <sup>16</sup> has suggested this as the reason why cellulose forms strong fibrous structures, while starch does not.

In making these models, the diameters of the carbon and oxygen were each taken as 1.5 Å., and the six atom rings were of the ordinary "puckered" type, with three atoms above and the three alternate atoms an equal distance below the plane of the ring.

## Mixtures of Nitrocellulose and Benzyl Cellulose with Common Plasticisers.

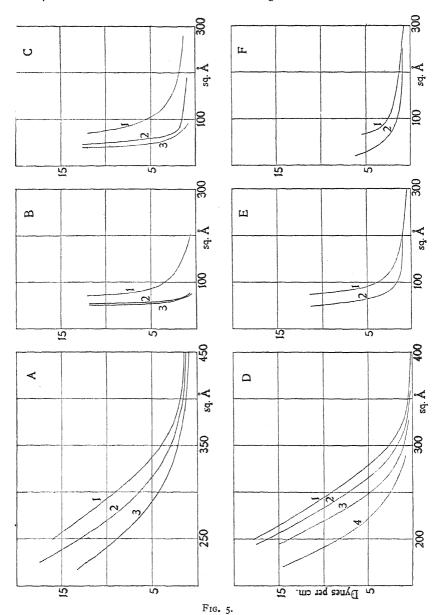
Castor oil, camphor, tricresyl phosphate, dibutyl phthalate, cellosolve, cellosolve acetate, and phenyl benzyl urethane, have been mixed (in solution) with nitrocellulose and benzyl cellulose, and the behaviour of the mixtures observed on spreading. Each of these plasticisers has also been spread separately. The benzyl cellulose mixtures were tried on water, the nitrocellulose on 2N soda. Ethyl acetate was used for the nitrocellulose mixtures, benzene-alcohol (5:2) for the benzyl cellulose.

Camphor, cellosolve, and cellosolve acetate, are too soluble to form films alone. In admixture with nitrocellulose or benzyl cellulose, the film after a minute on the water surface gives the same surface pressure at a given area that would be obtained with the cellulose alone occupying that area. Hence these water soluble plasticisers are completely dissolved out of the monomolecular films on water.

Phenyl benzyl urethane is too soluble in water to form a measurable film, and is completely dissolved out of a (partly spread) nitrocellulose film on water. On 2N soda, it is less soluble, and approximate measurements were obtained, which showed that the phenyl benzyl urethane forms a gaseous film (with fairly high adhesional corrections to the perfect gaseous state, the curve resembling that of dibutyl phthalate in Fig. 5). Mixed with nitrocellulose, one hexose group to one molecule of phenyl benzyl urethane, the area is reduced to about 40 sq. Å., all measurements were, however, very rough, owing to the film dissolving.

The results for castor oil, tricresyl phosphate, and dibutyl phthalate are shown in Fig. 5. The areas per molecule of the plasticiser, calculated by subtracting the area of the cellulose derivative from the total area of the film, assuming this to occupy its usual area per hexose group, are plotted horizontally, against dynes per centimetre. The composition of the mixtures is marked on the curves; "alone" means pure plasticiser, I: 3 means one molecule of plasticiser to 3 hexose groups in the cellulose, and so on.

The film of castor oil alone should probably be classed as liquid expanded. It tends, at low pressures, to a limiting area of 370 sq. Å. per molecule or 123 per chain, and shows very little surface pressure at greater areas. On 2N soda, the areas increase and no limiting area can be found. Admixture of cellulose derivatives reduces the area slightly, but not markedly so until 5 hexose groups are present for each molecule of the castor oil. The reduction of area never approaches near to that necessary to render the film a "condensed" film, in which the long chains of the oil would stand upright; this would require an area of about 60 sq. Å. per molecule.



- A. Castor oil and nitrocellulose on 2N NaOH.
   B. Tricresyl phosphate and nitrocellulose on 2N NaOH.
- C. Dibutyl phthalate and nitrocellulose on 2N NaOH.
- D. Castor oil and benzyl cellulose.
  E. Tricresyl phosphate and benzyl cellulose.
  F. Dibutyl phthalate and benzyl cellulose.

## Curves.

A1. alone.	B1. alone.	C1. alone.	Dr. Castor oil alone.	Er. alone.	F1. alone.
2. I:I.	2. I: I.	2. I:I.	2. I:I.	2. I:I.	2. I:I.
3. I:5.	3. 2:3.	3. 2:3.	3. I . 3.		
			4 T:5.		

Castor oil consists mainly of triricinolein, a triglyceride in which the chains have a hydroxyl group in the middle of the chain, and a double bond. The hydroxyl group would tend to make the chains lie flat in the surface; an area of 123 sq. A. per chain at low compressions is not far short of what would be expected for the eighteen carbon chain lying flat. But the films are readily compressed to much smaller areas, at which the chains must certainly be tilted to the surface. The probable structure of the castor oil film alone is that the molecules, at low compressions, are lying nearly flat, not necessarily quite flat, perhaps with some oscillation through tilted positions. Lateral compression easily forces the chains into tilted positions. Addition of cellulose derivatives, in considerable quantity, tends to squeeze the molecules into smaller space on the surface, probably through the lateral adhesion between the chains of hexose groups compressing the entangled molecules of oil; the hydrocarbon chains are never forced even approximately upright, however.

Tricresyl phosphate and dibutyl phthalate behave rather differently from castor oil. They form "gaseous" films, alone, in which the molecules are moving about individually and separately on the surface. The pressures are somewhat below those of a perfect gaseous film (FA = 400 at room temperature), indicating some degree of lateral adhesion between the molecules, but the adhesional corrections to the simple gas laws are not larger than are commonly found among surface films. Tricresyl phosphate shows more lateral adhesion than dibutyl phthalate. Dibutyl phthalate dissolved slowly. Tricresyl phosphate showed signs of collapse, with the ultramicroscope, above 5 dynes per centimetre pressure.

The action of cellulose derivatives on these two gaseous films is to reduce the area very considerably; since the large areas of the films of plasticiser alone are due to the independent motions of the molecules in the surface, it is clear that the single molecules of plasticiser become entangled among the heavy long chains, and cannot exert their normal kinetic pressure on the boundaries of the film. This simple explanation seems sufficient to account for the results; it would scarcely be possible for single, small molecules to maintain their normal bombardment pressure on a boundary of the film, if they were entangled among extremely heavy long chains, such as cellulose molecules.

The condition of the cellulose-plasticiser mixtures, spread out in a monomolecular film on a water surface, is so different from that of a varnish film containing plasticiser, that it should not be concluded that the mechanism of action of plasticisers in varnish films resembles the above. The motions of the underlying water molecules, in direct contact with every molecule in the surface film, probably dominate the phenomena by causing the observed behaviour of the film molecules, and there is nothing corresponding to this water in varnish films. It is interesting, however, to find that whatever compounds may be formed between nitrocellulose or benzyl cellulose and these plasticisers, these compounds are not stable enough to prevent a soluble plasticiser being completely dissolved out of the film by the water, which has, of course, complete facility of access to a monomolecular film.

#### Summary.

The spreading of methyl, ethyl, and benzyl ethers of cellulose, of cellulose nitrates, acetates, and esters with other fatty acids up to 18

carbon atoms in length, has been studied, by measurements of surface pressure and area, and by ultramicroscopic examination of the films. The ethers all spread completely on water, the esters incompletely, to films one glucose group in thickness. The esters mostly spread completely on twice normal caustic soda; nitrates containing more than about 12.6 per cent. of nitrogen spread incompletely even on this solution. The pressure-area curves of the spread films are of generally similar form for all the derivatives, above about 2 dynes per centimetre, with minor differences probably due to the size of the substituent groups. At low pressures there is sometimes a gradual, and sometimes a rapid, approach to the line of no pressure.

It is concluded that (a) the chains lie with every glucose ring nearly flaton the water, (b) the chains are flexible, and may be vibrating vigorously, in some cases, in the plane of the surface, at low compressions, (c) the differences in ease of spreading between different derivatives are partly due to the different adhesion of the esterified or ether groups to the water, and partly to the lateral adhesion between the chains in the solutions of the cellulose derivatives. There appears to be a much greater tendency of the cellulose nitrates and acetates to aggregate side by side in solution, than of the ethers. In no case, except possibly cellulose itself, do "micelles" or bundles of parallel chains exist in the solutions, of sufficient stability to resist extensive disruption by the spreading action of the water.

Alkyl nitrates with long chains spread very imperfectly on water or soda, the adhesion of the nitrate group to the water being of the same order

of magnitude as that of the methyl-ether group.

The spreading of some common "plasticisers" has been studied alone, and mixed with benzyl celluloses and nitrocelluloses. Plasticisers which are slightly soluble in water are dissolved out of the film; insoluble plasticisers have the motions of their molecules impeded by the cellulose chains.

My thanks are due to the colleagues mentioned above for gifts of material; to the Research Department of Imperial Chemical Industries, Ltd., Ardeer, and Mr. F. D. Miles, for their constant interest and advice; and to the Government Grant Committee of the Royal Society for a grant which defrayed the cost of part of the apparatus used.

The Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London, W.C. 1, and Imperial Chemical Industries, Ltd.

#### GENERAL DISCUSSION.

**Dr. J. R. Katz** (Amsterdam) said: The interesting experiments of Dr. Adam confirm very well the experiments on the spreading of cellulose derivatives on a water surface published by Mr. P. J. P. Samwel and myself in 1928 and 1929. We found to our surprise that methylcellulose and ethylcellulose spread in a monomolecular film to a degree approximately of the thickness of one hydrocarbon chain. Dr. Adam finds numbers of the same kind.

These experiments in 1928 indicated that the polymerisation of cellulose, starch and other polysaccharides must either lead to long molecules in the form of a chain or to molecules in the form of a thin sheet,

<sup>&</sup>lt;sup>1</sup> Naturwiss., 16, 592, 1928; Ann. Chem., 472, 241, 296, 1929.

but that there cannot be three-dimensional association. Since then we have got many arguments for a long chain form.

Moreover, these experiments seemed to show that the micellae in colloidal solutions of cellulose derivatives cannot be three-dimensional, as was generally supposed at that time. They corroborated the view, then defended almost alone by Professor Staudinger, that such solutions may be truly molecular disperse with very large molecules. In the paper of Dr. E. H. Büchner 2 there is new evidence supporting this view, which now finds much more adherence.

As to the question whether the acetates are spread to real monomolecular films, I must make a certain reservation in respect to the value of the submicroscopical examination of surface films according to the method of Zocher and Stiebel. I have now got a good deal of experience with this method, and think that it can easily lead to incorrect conclusions if we lay too much stress on slight inhomogeneities we see in the surface films. The method has the disadvantage of being too sensitive, so that it can clearly show the existence of inhomogeneities, which give errors in the areas found, lying well within the experimental limits. What we really want is a quantitative method, showing us what percentage of the substance in the film is not monomolecularly spread.

Until we have such a quantitative method, we must control our submicroscopical observations by measuring the area of closely allied substances. If all these measurements agree well we may feel confident about their value, even if we see small inhomogeneities under the ultramicroscope. In the case of ethylcelluloses, for instance, it is very remarkable that the areas found by Mr. Samwel and myself, in the case of good technical ethylcelluloses and of the very pure crystalline preparations of Professor Kurt Hess, agreed within a limit of error of 10 per cent. This indicates that in the case of ethylcelluloses the faults in homogeneity which may exist in the technical preparations do not invalidate the results of the investigation.

In the case of acetylcelluloses also (both with 2.9 and with 2.25 acetyl groups per  $C_6H_{10}O_5)$  we came to the same conclusion, in comparing good technical acetates and pure crystalline acetylcelluloses of Professor Kurt Hess. Within a limit of error of 10 per cent. we found the same areas in both cases. I must add that I chose the acetylcelluloses very carefully, so that only those which dissolved easily and entirely without any insoluble residue were used in our experiments; if the solution itself contains larger particles than necessary I would reject it for a spreading experiment. I fear these very necessary precautions have not always been taken by others.

With these precautions, we found an area of about 40 square Angstrom units for all acetylcelluloses. The same number was found in the case of the acetates of the polysaccharides starch, inuline, lichenine, and in the case of disaggregated acetylcelluloses (such as the "abgebaute Acetylzellulose" of Professor H. Pringsheim and "hexacetylbiosane" of Professor Kurt Hess). Where we always found approximately the same area we consider these numbers as valid. We were corroborated in this opinion by the ultramicroscopical examination of the acetylcellulose films by Zocher and Stiebel and by ourselves. Inhomogeneities can be almost entirely absent, and yet the films give the ordinary area.

I do not want to leave this subject without expressing my admiration

for the measurements of Dr. Adam on these cellulose films at very low pressures, and for his work on spreading in general. His method for measuring these very low pressures in surface films has been the result of his great experience on the subject, and is valuable in the case of cellulose derivatives in showing us what kind of films they are forming, probably solid and not gaseous films. As to the explanation of the strong compressibility of these films at high pressures, I feel some doubt whether these molecules can be bent as strongly as Dr. Adam accepts. Does not rotation around the long axis of the molecule come into play too in explaining the compressibility?

**Dr. Adam,** in reply to Dr. Katz, said: I think my results for the area of acetyl cellulose agree pretty well with those found by Katz and Samwel; the question is, are they fully spread films or not? Zocher and Stiebel thought they were fully spread, but I am inclined to think that they are not, having found some appearance of unspread material with the ultramicroscope. At present I see no way of obtaining a quantitative estimate of the proportion of material spread, except to assume a certain area per molecule for the fully spread film, and using this, to calculate from the apparent area per molecule what proportion of the whole is spread. As most of the celluloses show about the same area, I am inclined to assume the acetates occupy the same space as the others, when fully spread. This gives about 70 per cent. spreading.

It seems to me quite likely that Dr. Katz's suggestion that the hexose groups rotate about their long axis, so as to occupy less space on the water surface, is one of the ways in which the compressibility of the film is obtained. Unfortunately experimental methods for distinguishing between tilting and rotation do not yet seem to be available.

**Professor H. Mark** (Wien) said: This very careful examination of the compression-curves shows in a rather convincing way the flexibility of the long chain molecules. A certain amount of flexibility seems to be necessary for any reasonable explanation of the reason why these chains form bundles and micelles. If they were quite stiff they could not lie parallel to one another so rapidly as is actually observed, if one precipitates cellulose derivatives from their solutions.

Mr. E. G. Cox (Birmingham) said: Dr. Adam's suggestion that the lateral adhesion of cellulose ester chains is greater than that of cellulose ethers is supported by the fact that acetylated polysaccharides are obtained crystalline much more frequently than are the methylated substances. Further support is provided by the optical properties of cellulose and its derivatives; the highest values of the refractive index perpendicular to the fibre axis are shown by native cellulose and highly nitrated cellulose, indicating that in these two substances, which are the two which show the least tendency to spread on water, the lateral association of the primary valency chains is probably greatest.

With regard to the difference in spreading properties of starch and cellulose derivatives, it may be pointed out that it is only by choosing arbitrarily one of the large number of possible strainless configurations for the glucose ring (cf. Haworth, Constitution of Sugars, chap. X.), that cellulose is enabled to form a straight chain and starch is not. By assuming another model, equally valid from a chemical point of view, the reverse result could be obtained. X-ray studies of crystalline carbohydrates carried out in Birmingham have shown that the pyranose ring cannot have the Sachse trans form which it is frequently assumed to have. The evidence at present favours a ring in which the five

carbon atoms are in a plane, with the oxygen atom displaced out of it; further, it appears that in  $\beta$ -glucose the reducing group is on the same side of the ring as the oxygen atom. On constructing models on these lines, it is found that whereas a chain of  $\beta$ -glucose units (i.e., cellulose) can be made to assume a straight form, a chain of α-glucose units (i.e., starch) cannot be rectilinear. Thus the spreading experiments and the X-ray evidence lead to the same conclusion.

Dr. W. B. Lee (Manchester) said: Dr. Adam's experiments are of great interest in connection with the problem of determining the range of molecular attraction. It seems that they prove beyond reasonable doubt that the cellulose derivatives mentioned in the paper spread on water to form layers one molecule thick, and that these are very stable. But I should like to suggest that the work be pushed further in an attempt to produce stable bi- or poly-molecular films. This will in all probability require considerable refinements of technique and, in particular, the exclusion of dust particles by the use of purified air. Precautions of this kind will be necessary in order to avoid the presence of nuclei about which the molecules in the upper layers might condense in droplets since it is to be expected that the second and successive molecular layers will be much less stable than the first.

Nevertheless, such work should be well worth while as a contribution to the much debated question of the range of molecular attraction since, if it can be shown that monomolecular layers are in general the only possibility for stable films, some progress will have been made towards a solution of the difficult problem of adhesion. The choice of a mechanism of adhesion at present appears to lie between the wave mechanical explanation which necessitates a close approach of adhering "surfaces" to within a distance of the order of a few atomic diameters on the one hand and, on the other hand, the older classical explanation based on the postulation of van der Waals' forces which might act over distances of entirely different magnitude.

The ideas embodied in the new quantum and wave mechanical theories of matter and energy have now, for the first time in the history of science, provided us with a more or less intellectually satisfying conception of what previously went by the name of "residual affinity," "secondary valency," "molecular force fields" or some similar term. But any gain in clarity of perception is necessarily accompanied by a sharp limitation of the range of these forces and I find it difficult to conceive effective adhesional ranges greater than about 10 Å. It is of course possible that adhesion may take place between "surfaces" more widely separated than this, but I think that in such cases it will be necessary to postulate the existence of molecular chains or oriented aggregates of both pure and foreign matter to play the part of "adhesive" and transmit the relatively short range forces.

I assume that no investigator may be quite certain that he has excluded dust (and accompanying contamination) from interfaces. I drew attention to the importance of this in connection with prisms and lenses, 4 after using elaborate interferometry, purified air, optical gauges of the highest precision obtainable, and various optical and mechanical methods.

Purified air frequently may do more harm than good if dust particles in containers, etc., are set in motion. It has been claimed that dust particles cannot be eliminated entirely even with high vacuum technique. The question is, what errors may dust particles produce in the real or apparent "joint strength"? This depends upon the way in which the interest is made and may be preclicible.

joint is made, and may be negligible.

In this connection it is perhaps only fair to admit that, in my opinion, no published investigations on adhesion have yet established that "long range" forces do not exist. But the general tendency is by improved experimental technique to decrease the distance to which (say) optically worked surfaces may approach in supposedly pure air or pure liquids with the result that reported equilibrium separations of the order of several  $\mu$  become more and more improbable as time goes on!

Dr. Adam is well aware that the suggestion regarding mono- and bi-molecular layers is made as a precautionary measure. One likes to be quite certain that Leslie's explanation of the spreading of a pure liquid (without solvent) on water is incorrect. I am in favour of short range forces as a general rule, but I think there is a "transmission effect" (whether through the agency of van der Waals' molecular pressure, electrical polarisation, dust, or other cause), in certain special cases.

## THE MOLECULAR AGGREGATION OF NITRO-CELLULOSE.

By F. D. MILES.

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The long chain molecule is now accepted as the best explanation of the chemical and physical properties of cellulose and its derivatives. The results of X-ray investigation correspond to structures which consist of parallel arrangements of these chain-molecules, but there is still some uncertainty about the way in which the chains are associated with each other throughout the fibre. In less organised solid forms such as films the association is less definite, and little regarding it is known. Divergent views are still held of the nature of solutions of those derivatives which can be dispersed, for the dissolved particle may be either a single molecule, or may consist of a number of associated molecules.

In the nitrocelluloses hydroxyl groups have been replaced by nitrate groups, but with the exception of the trinitrate—the final member of the series—the replacement is incomplete. The constitutional problem has therefore a two-fold form, for before the aggregation of the chain-molecules can be fully understood, it will be necessary to know the way in which the nitrate groups are distributed among the molecules. Partly on account of their intrinsic interest, partly on account of their technical importance, the nitrocelluloses have been more extensively studied than most other cellulose derivatives, but agreement on these questions of molecular form and aggregation, discussion of which is the object of this paper, does not seem so far to have been reached.

It is generally supposed that in organic fibres the chains are arranged parallel to each other in micelles, and that each micelle is structurally discontinuous with those adjacent to it. It is often assumed that inside each micelle the structure is perfect. The dimensions of the micelle can be estimated from the broadening of the X-ray lines which is caused

by the bundles being so small that the diffraction by the atoms in them is incomplete. The spots produced by planes parallel to the fibre axis are more diffuse than the others, and from this it follows that the micelles are narrow in comparison with their length along the axis. This conception of discrete micelles cannot be realised without difficulty, especially when the number of molecules in the micelle is assumed to be small, and the question may be asked whether it should not often be modified. The matter has been discussed by Astbury and Woods, who believe that the bounding surfaces are not sharply defined, but that the micelles are to some extent entangled with one another by pseudo-crystalline growths and shared molecular chains.

Broadening of the X-ray lines may be caused not only by the presence of small constituent particles but by lattice irregularity or distortion. Hengstenberg and Mark <sup>2</sup> considered that micellar division played the larger part, because the intensity of the radiation scattered diffusely by cellulose was only slight, but they stated that no certain method was known by which the two effects could otherwise be distinguished. It does not seem impossible that the lateral interlocking of the corresponding atoms of contiguous long chains is, throughout the fibre, less exact than has usually been assumed.

Cellulose has a comparatively exact structure, probably on account of the strong lateral adhesion, but in many of its derivatives this adhesion is less, the diffusely scattered radiation is more marked and the effect of lattice irregularity may be expected to be greater. It is interesting to consider, from this point of view, the absorption of a liquid or of its vapour by such a derivative. If the hypothesis of division into discrete micelles is adopted, there may be said to be two principal processes by which a liquid or its vapour may be taken up. The molecules may (I) find their way in between the chains and cause the spacings to expand, giving rise in many cases to the formation of definite structural complexes of the two substances, or (2) they may pass in between the micelles, causing them to separate to a greater distance. But if the crystalline structure is inexactly co-ordinated, there may be no very sharp distinction between intra- and inter-micellar swelling. Whether the micellar boundaries are considered to be surfaces of sharp structural discontinuity, or whether they are formed by the regions in which the interlocking of the chains is least perfect, the forces holding the molecules together there, although less organised than those acting where the structure is more perfect, must be of the same kind. A molecule which has sufficient chemical affinity with the substance of the fibre to enter an intermicellar region may be expected to penetrate the micelle itself to an extent depending on the degree of disorganisation of its structure. By such a process of penetration subdivision of the micelle can readily be imagined to take place.

In such an inexactly adjusted crystalline structure there will be differences of free energy from one point to another, and it is possible that these differences may be of importance in a chemical reaction between the chain molecule and another molecule which can penetrate between the chains (as nitric acid penetrates cellulose). Such differences of energy may cause the reaction to occur in one region more readily than others, and to proceed in an apparently random way, the proportion of the fibre affected being controlled by the temperature and the activity of the reagent.

<sup>&</sup>lt;sup>1</sup> J. Text. Inst., 23, T132, 1932.

#### Nitrocelluloses and their Preparation.

The only nitrate of cellulose which is structurally definite appears to be the trinitrate. The characteristic X-ray diagram of this substance, first obtained by Andress 3 and Naray-Szabo and von Susich, 4 is given by nitrated ramie containing considerably less nitrogen than the theoretical percentage for complete nitration (14·14). To obtain a fairly welldefined diagram it is necessary either to nitrate with a nitric-sulphuric acid mixture containing more nitric acid (45 per cent.) than is usual in technical practice (20-25 per cent.) or to carry out the process in nitric acid vapour, 5, 6 or if mixed acids of lower nitric acid content are used, to boil the product with acetic acid or methyl alcohol.7 By nitration in an acid mixture of suitable composition a nitrocellulose of any nitrogen content less than 14 per cent. can be made, but no evidence of any

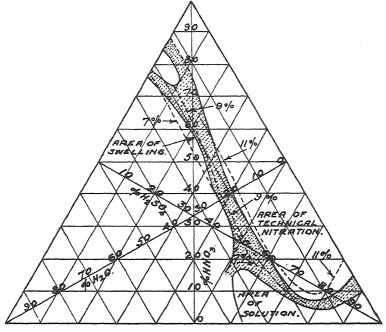


Fig. 1.

definite compound other than the trinitrate has ever been obtained. It does not seem unreasonable, however, to expect that the difference in the configuration of the three hydroxyl groups in the glucopyranose residue should make possible the formation of either the mono- or the dinitrate, if the appropriate conditions could be realised and rigidly held constant.

Although there is no sharp chemical discontinuity in the series of nitrocelluloses, an important and peculiar feature nevertheless enables an approximate division of the products to be made into three

<sup>3</sup> Meyer and Mark, Ber., 61, 594, 1928.

<sup>&</sup>lt;sup>4</sup> Z. physikal. Chem., 134, 264, 1928. <sup>5</sup> Miles and Craik, J. Physical Chem., 34, 2607, 1930.

<sup>6</sup> Nature, 123, 82, 1929.
7 Trogus and Hess, Z. physikal. Chem., 12B, 268, 1931.

classes. It is not possible to obtain by any recognised method (even by nitration in nitric acid alone) a nitrocellulose containing about 9 per cent. of nitrogen without swelling and disintegration of the fibre. On the triangular diagram which may be used to plot the compositions of all mixtures of nitric acid, sulphuric acid and water (Fig. 1), the region in which are formed products showing these effects after washing, has the form of a band which crosses the whole diagram, and the line representing mixtures which nitrate to 9 per cent. of nitrogen lies wholly within the band. At its extremities the band widens out to enclose two areas representing mixtures of high nitric and sulphuric acid content respectively, in which the partially nitrated fibre completely dissolves.8 This area is important in any view which may be taken of the whole range of nitration phenomena. Some points of its significance will be discussed later. For the present it is sufficient to note that we may divide nitrocelluloses into three classes with reference to the position on the chart of mixed acid composition of the acids in which they are made: (I) those containing less than about 7.5 per cent. of nitrogen, showing unimpaired fibre structure, insoluble in all solvents, (2) those containing from 7.5 to about 10.5 per cent. of nitrogen, showing more or less destruction of the fibre, and either swelling or partially dissolving in acetone, and (3) those containing more than 10.5 per cent. of nitrogen, quite fibrous, and completely soluble in acetone and other solvents. All nitrocelluloses of technical importance belong to the last class.

# The X-ray Investigation of Nitrocellulose and the Theory of the Nitration Process.

Herzog and Naray-Szabo <sup>9</sup> and Naray-Szabo and von Susich <sup>10</sup> were the first to form an idea of the structure of the nitrocelluloses from the results of X-ray work. They claimed that all were to be regarded as mixtures of trinitrate and unchanged cellulose. Miles and Craik, <sup>11</sup> after examining series of nitrocelluloses and of their denitration products, were unable to confirm this conclusion. Trillat <sup>12</sup> also worked with a wide range of material in both film and fibre forms, and was of the opinion that from 2·17-6·17 per cent. of nitrogen the preparation contained unaltered cellulose and amorphous nitrated material, that from 10·4-12 per cent. a mixture of amorphous material and crystalline trinitrate was present, and that, for more than 12 per cent. of nitrogen, trinitrate in a pseudo-crystalline condition was the principal constituent. He believed the amorphous and less nitrated constituent to be made up of cellulose chains each nitrated incompletely, and discussed the several general arrangements the nitrate groups might have in such chains.

The nitrocelluloses examined by Miles and Craik <sup>13</sup> were for the greater part made in acid mixtures having a nitric-sulphuric acid ratio of (I:I) since the use of these mixed acids had been found to lead to better defined X-ray diagrams than others of more usual technical composition. To account for the results they suggested a conception which may be reproduced here. Certain complications arising from peculiar features of the diffraction diagrams will be discussed later.

 <sup>8</sup> Miles and Milbourn, J. Physical Chem., 34, 2598, 1930.
 9 Z. physikal. Chem., 130, 616, 1927.
 10 Loc. cit., 4, 367.
 11 Nature, 123, 82, 1929.
 12 J. Physique et Radium, (7), 1, 340, 1930.
 13 J. Physical Chem., loc. cit.

Since in the first stage of nitration the only diffractions observed were those of almost completely mercerised cellulose, it was suggested that either on account of structural discontinuities or by the penetration of the nitrating acid along certain planes of the crystal structure only the hydroxyl groups in the internal surface of the fibre were nitrated, the interior of the micellar units of cellulose being unaffected. As the nitrating mixture is made more concentrated a progressively greater area of surface is affected until, in nitrations of the second class, the number of unaltered cellulose chains becomes too small for definite diffraction and the micellar arrangement is almost entirely broken down. Just as in the case of tripalmityl-ramie, recently described by Hess and Trogus. 14 the organised arrangement of chains is almost but not quite destroyed. The parallel arrangement of chains cannot be altogether lost, for although this nitrated material of Class II. gives only diffuse halos the cellulose obtained from it by denitration gives reasonably sharp diagrams.

The swelling and the breakdown of the micellar arrangement take place in nitrations of the third class, but to a diminishing extent as the dilution of the acid diminishes. The chains are at first easily accessible to the action of the nitric acid, and as the concentration of the acid is increased (from one nitration to another) nitrate groups are attached to the chains in increasing number, in all probability with only approximate regularity, so that definite crystallisation is at first difficult, but becomes less so as the nitrate groups become more numerous until, at about 12-8 per cent. of nitrogen, the definite diagram characteristic of the trinitrate appears. Above this limit of nitrogen content, no change in the diagram has been noticed.

In the first phase, therefore (nitration to 7.5 per cent. or less), the reaction was supposed to be heterogeneous but in the later phases to be permutoid. The essential feature of the conception is that in nitrations of Classes II and III, the nitrate groups are distributed among the chain molecules, either at random or in a number of different arrangements which cannot be distinguished, in either case so that the chance is small that any one molecule will be completely converted into trinitrate before the rest.

An explanation of the nitration process, which differs in essential points from that already outlined, has been put forward by Hess and Trogus. 15 These workers prepared their nitrocelluloses (varying in nitrogen content from 7 to 13.5 per cent.) by the somewhat unusual method of nitrating ramie for periods varying from one minute to twenty hours in a single anhydrous acid mixture containing 29.7 per cent. HNO3 and 70.3 per cent. H2SO4. From the results of this and other similar studies of the formation of cellulose esters and ethers, they have come to the conclusion that the permutoid reaction must be excluded from the discussion; the micellar surface reaction must be accepted as the true type of reaction (Idealreaktion) for cellulose. It seems doubtful whether the examination of the products of nitrating for varying times is likely to throw much light on the standard process of nitrating to an end point in any other acid mixture than that actually used, but the conclusions are intended to be generally applicable, for it is stated (loc. cit., p. 216) that evidence which seems to favour the permutoid type of reaction can be interpreted in favour of the heterogeneous type, if the particular conditions of the reaction are taken intoaccount. For instance, the equilibrium between nitrocellulose and nitrating acid which has been discussed (for Class III) by Berl and Klaye 16 is to be ascribed to variations in the effective superficial area of the micelles which arise from changes in their accessibility or in their shape and size. The nitration proceeds inwards from the surface of the micelle, leaving the cellulose core unaltered. The X-ray diagrams are therefore those of mixtures of cellulose and its trinitrate, as had previously been maintained by Herzog. The persistence of the cellulose diffractions in the diagrams of the less nitrated products and the late appearance, at the other end of the series, of those of the trinitrate, is accounted for by the progressive extension of the trinitrate zone into the micelle.

There are therefore two opposed ideas of the formation and constitution of the important and useful varieties of nitrocellulose belonging to Class III. According to one, these substances are built up of cellulose chains, some of which are completely nitrated, the others not at all; in terms of the other they consist of chains all of which are nitrated, but incompletely. A decision is important from many points of view. Before attempting one it will be advisable to discuss some of the features of the reaction between cellulose and nitric acid.

#### Some Phenomena Related to Nitration.

The Formation of the Knecht Complex.—The X-ray diagram of fibres obtained by denitrating nitrocellulose of Classes I and II shows them to consist almost entirely of mercerised cellulose. It is probable therefore that some constituent of the nitrating mixture must have penetrated the whole structure. Now since Katz and Hess, 17 and more recently Andress,\* 18 have shown that the nitric acid-cellulose complex to which Knecht 19 gave the formula C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>. HNO<sub>3</sub> has a characteristic definite structure and yields mercerised cellulose on treatment with water, it is difficult to avoid the conclusion that in the first and second kinds of nitration the nitric acid must penetrate the micelle. A ramie bundle, kept wet with nitric acid of from 65 to 75 per cent. gives the diagram of the Knecht compound while nitration is beginning. In 75 per cent. acid, ramie is nitrated to a nitrogen content of 5 per cent. in an hour. (†) If the further progress of the reaction in nitric acid of higher concentration is heterogeneous, the reacting solid cannot be cellulose, for intramicellar penetration and the formation of a new structure have already occurred.

We do not yet know whether this nitric acid in structural combination with the cellulose plays any part in the nitration, but in view of the possibility which has been suggested in the introductory remarks, that a reaction may occur between favourably situated groups in the structure and a reagent which is able to penetrate between the chains, it seems to be by no means certain that even in the weakest acids nitration is a surface reaction, or in any true sense heterogeneous.

Swelling during Nitration.—A critical region in the nitration field is the median zone in which the swelling effects of nitration reach

<sup>&</sup>lt;sup>16</sup> Z. ges. Schiess u. Sprengstoffwesen, 2, 403, 1907.

<sup>&</sup>lt;sup>17</sup> Z. physikal. Chem., **122**, 126, 1926.

<sup>18</sup> Ibid., 136, 279, 1928.

\* Andress found that the composition corresponded to 2C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>HNO<sub>3</sub>.

† Results obtained at Ardeer, as yet unpublished, are designated thus throughout the paper.

a maximum. Recent experiments (†) have shown that the preferential adsorption of nitric acid which occurs when cellulose is immersed in mixtures of this acid with water, or with water and sulphuric acid, rises as the water content is reduced and reaches a maximum in the swelling area, i.e. when the nitration has reached about 9 per cent. abstraction of acid from the solution is of course distinct from the consumption of acid in the chemical reaction of nitration. The case of nitric acid-water mixtures is the simpler. The absorption begins to be considerable just when the nitration begins and rises as the acid concentration increases. Experiments cannot readily be made over the whole range, for in acids of concentration 78-95 per cent. HNO<sub>2</sub> the fibre tends to dissolve altogether, 20 but it is apparent that the absorption reaches its highest value when the nitrogen content is about 9 per cent. and the swelling is greatest. This varying absorption can be viewed as depending partly on the varying degree of nitration of the cellulose chains, and partly on the activity of the nitric acid.

On the other hand, if the swelling in this region is not that of partially nitrated molecules able more or less to separate from each other, but of cellulose micelles nitrated on the outside only, it must be associated with some tendency to swell of either the trinitrate on the peripheral surface of the micelle, or of the cellulose core, or of both. The trinitrate layer on the micelle must always be permeable to nitric acid, for this is an inherent necessity of the micellar mode of nitration-which could not otherwise proceed. Now unswollen trinitrate made in a more concentrated acid mixture does not swell when placed in a less concentrated acid mixture having the same nitric-sulphuric acid ratio but containing sufficient water for the swelling of fresh cellulose. To show that the presence of sulphuric acid has nothing essential to do with this an extreme instance may be noted. Trinitroramie becomes rather brittle but does not swell when immersed in 83 per cent. nitric acid \* which, while it partially nitrates fresh cellulose, soon dissolves the product entirely. † It is difficult, therefore, to associate the swelling with the presence of the trinitrate. Nor can the claim be made that the cellulose core is responsible, for the swelling is always accompanied by high absorption of the nitric acid from solution, which would involve an abnormally high concentration inside, or on the surface of the micelle, and this would result only in nitrating it.

The Nitration Equilibrium.—There seems to be an important difference between nitration and the formation of the acetates and of other derivatives in the fact that the degree of conversion can be controlled through the composition of the nitrating mixture. Within a considerable range a definite nitrogen percentage is reached for every mixed acid composition, and it is difficult to avoid the conclusion, in view of general technical experience, the investigations of Berl and his collaborators, <sup>21</sup> and the recent work of Demougin and Bonnet <sup>22</sup> that an equilibrium is reached, however slowly in the direction of decreasing nitration, for the final degree of nitration is independent of time and can

<sup>&</sup>lt;sup>20</sup> Miles and Milbourn, loc. cit., 2603. Compare also Vielle, Mémorial des Poudres. 2, 212, 1884-1880.

Poudres, 2, 212, 1884-1889.

<sup>21</sup> Berl and Klaye, loc. cit.; Berl and Berkenfeld, Z. angew. Chem., 41, 130, 1028

<sup>&</sup>lt;sup>22</sup> Mémorial des Poudres, 147, 1930-31.

<sup>\*</sup>On standing in the acid, however, the material is slowly denitrated and swelling becomes apparent.

<sup>†</sup> See note on p. 115.

be changed to another constant value, either higher or lower, by immersing in another mixture. It is well known that celluloses from different sources nitrate to practically the same extent. Viscosity of the cellulose has little influence.

If the permutoid reaction is to be excluded, as the micellar theory proposed by Hess and Trogus would demand, these facts become difficult to explain. If the reaction to trinitrate is the only one and occurs only at the surface of the core of the micelle, it is necessary to account for the apparent equilibrium by the hypothesis of some surface force which opposes the liberation of the free energy of the chemical reaction, although it might be expected rather that the reaction should occur more readily as the cellulose core became smaller. That the core can be regarded as having any real surface in the usual sense is not probable, for on the basis of 60 molecules in the cross-section of the micelle of ramie cellulose (the figure to which Mark and Hengstenberg's determinations lead) there would be only fifteen in the cellulose core of a nitro-cellulose containing 12 per cent. of nitrogen, or four in a single plane if the core were a square prism.

The Effect of Stabilisation.—Trogus and Hess made the important observations 23 that unstable trinitroramie which had merely been washed with water after removal from the mixed acid gave a much less definite diagram than that of the same material after boiling in 50 per cent. acetic acid \* or in methanol, and that if the X-ray diagram were made while the fibres were wet with the nitrating acid, it was still less definite except for the principal equatorial spot, which indicated a spacing (7.41 Å) different from that of the stabilised material (7.30 Å). Stabilised material wetted with the nitrating acid gave the same spot at a position corresponding to a still larger spacing (7.60 Å). This swelling effect is most probably due to intramicellar penetration of nitric acid. Much of the disorganisation (as distinct from alteration of spacing which the trinitrate undergoes) is, however, due to the sulphuric acid and some caution seems to be necessary in coming to an opinion about the nature of nitration solely from the examination of the products when a large proportion of sulphuric acid has been used. The fact may be mentioned that trinitro-ramie made in nitric acid vapour gives a sharp point picture with no washing whatever. (†)

#### The Existence of two Structurally Different Nitrocelluloses.

The nitrocelluloses examined by Miles and Craik gave diffraction spots which moved slightly inwards-indicating continued increase of the spacings—as the nitrogen rose from 10-12-8 per cent. At this point a sudden change to the trinitrate type of diagram occurred manifested by large changes (9-15 per cent.) of the spacings, all in the same direction. At 12.9 per cent. the change was complete. Similar behaviour has since been observed for nitrocelluloses in the same range of composition but made with less nitric acid (†). There seem, on this evidence, to be two types of nitrocellulose structure, and in the case of the first series mentioned 12.8 per cent. is a critical point. Trillat,24 whose later work on films will be mentioned immediately, found a corresponding point at 12.95 per cent. of nitrogen.

<sup>&</sup>lt;sup>23</sup> Z. physikal. Chem., 12B, 268, 1931.

<sup>&</sup>lt;sup>24</sup> J. Physique et Radium (7), 2, 66, 1931.

\* It has been found difficult to effect a stabilisation of fibrous ramie which would be considered technically satisfactory by this, or indeed any similar process. † See note on p. 115.

The slight increases of spacing between 10 and 12.8 per cent. could not be traced to the superposition of the diffraction of the ordinary trinitrate and of either form of cellulose in varying proportions, but Hess and Trogus 15 have attributed them to the superposition of the diffraction of two forms of trinitrate, one related to the ordinary, the other to the mercerised variety of cellulose. This explanation does not cover all the data. In particular, one of the spots (corresponding to a spacing of 3.86 Å) moves in a direction opposite to that which would agree with interference by any possible diffraction of the normal trinitrate. The explanation originally advanced—that the structure can expand as the nitrogen increases to 12.8 per cent.—seems, therefore, to offer the best account of the facts. We may have in this range something corresponding to an isomorphous series, perhaps with cellulose chains of different configuration built into the structure. The relation of these two types of structure to the two forms of cellulose does not yet appear clear. The composition of the nitrating acid and the temperature of nitration are both of influence. The lower the temperature and the proportion of nitric acid the greater is the proportion of ordinary cellulose in the product of denitration.

It is possible that there may be a connection, though not necessarily a causal one, between such a change in structure which has been observed at 12.8 per cent. of nitrogen and certain other properties. Jenkins and Bennett 25 and Rubenstein 26 found during their studies of the sorption of solvent vapours by nitro-cellulose that the sorption of acetone, methyl ethyl ketone, methyl and ethyl acetate increased as the nitrogen content of the nitrocellulose rose from 10 per cent. to a maximum at 12 per cent. and then decreased as the nitrogen increased to 13.4 per cent. This is what should be expected if a nitrocellulose of the trinitrate type (Trinitrate I in Hess and Trogus' formulation) had even a slightly lower capacity for sorption than one of the other type (II).

#### Nitrocellulose in Solution.

The idea of the solution of long chain compounds which has been so long advocated by Staudinger—the single chain molecule as the solution unit—is now very widely accepted. We know from the recent work of Trogus and his collaborators <sup>27</sup> that the trinitrate of cellulose forms two well-defined structural compounds with acetone, so that even in the solid state intramicellar penetration of the solvent is complete. Recent work (†) has shown that in aqueous acetone, even before the new compound is detectable in the fibre, this penetration is evident, and the spacings of the nitrocellulose have begun to change. As the critical solution concentration of acetone or "compatibility point" 28 is approached the absorption of solvent continually increases, so that the elements of the fibre which eventually dissolve are already highly solvated and therefore can retain little if any of their lateral adhesion.

The fact that the numerous cellulose derivatives investigated by Katz and Samwel 29 gave monomolecular films when spread on water by the Langmuir-Adam method seems to be decisive in favour of the

J. Physical Chem., 34, 2318, 1930.
 Z. physikal. Chem., 16B, 360, 1932.
 Craik and Miles, Trans. Far. Soc., 27, 8, 1931. <sup>26</sup> Ibid., 2330, 1930.

<sup>&</sup>lt;sup>29</sup> Annalen, **472**, 241, 1929. † See note on p. 115.

molecular dispersion in solution. The recent work of Dr. Adam (who has kindly allowed reference to his results) shows that nitrocellulose spreads in the same way on 2N sodium hydroxide solution, and that within a considerable range of nitrogen content (10.9-12.6 per cent.) there is no very great difference in the area to which the films would approximate at zero pressure. Now if nitrocelluloses are really constituted as the micellar theory of nitration of Hess and Trogus would demand, when solution of a nitrocellulose takes place either the micelle must solvate and disperse as a whole, or the trinitrate must be detached from the outside leaving the core of cellulose, because there is no reason whatever to suppose that the molecules in the core of cellulose could disperse. If the first alternative is adopted, it seems impossible to account for the spreading to the thickness of one molecule, if the second, only the trinitrate could spread, and the measured area, in the case of the nitrocellulose of 10.4 per cent., would be less than that actually found by 35 per cent., a defect which could hardly escape detection.

By means of an extension (†) of a fractionation process already described, 30 any ordinary nitrocellulose which is soluble in pure acetone may be separated into as many fractions as are desired. fractions show a wide range in viscosity, but although the process has been carried out with many very different nitrocelluloses in no instance has the extensive variation of nitrogen content, among the fractions from the same starting material, exceeded about 0.3 per cent. No evidence of the presence of trinitrate in solution has been obtained in this way. In the extreme instance (†) of a nitrocellulose which was nitrated for 5 hours at 0° C. and was soluble in pure acetone only to the extent of 72 per cent. there was only the slightest difference between the degree of nitration of the soluble and insoluble parts, for the nitrogen percentage of the former was found to be 10 01 per cent., that of the latter 9.92 per cent.\* To account for these facts on the basis of the mixture theory of the composition of nitrocellulose the micelle must be adopted as the solution unit, in face of the contrary indications of the work of Adam and of Katz and Samwel.

To adopt the molecular disperse theory for nitrocellulose solutions is by no means to deny that molecules may be associated with each other in solution. Staudinger <sup>31</sup> has pointed out that nitrocellulose solutions show variations from Poiseuille's law which are exceptional for a cellulose derivative and point to a certain degree of structure in the solution. It is possible that this association may be in part derived from the original structural arrangement of the fibre, because if nitration is a change affecting all the chain molecules, but in a random, or an apparently random way there will be a certain chance that here and there two or more chains have sufficient hydroxyl groups together to maintain their adhesion in opposition to the action of a solvent whose affinities are for the nitrate groups. This would be most likely to happen at a low degree of nitration, but so far we have no certain evidence of it.

<sup>&</sup>lt;sup>30</sup> Craik and Miles, *loc. cit.*, 1. <sup>31</sup> Ber., **63**, 2329, 1930.

\* If the method of nitrating for a very short time in a concentrated mixed acid is employed, much greater differences between the nitrogen contents of the soluble and insoluble fraction are to be expected. Data which illustrate this point have been obtained by Atsuki and Ishiwara (*Proc. Imp. Acad. Japan*, 4, 382, 1928).

† See note on p. 115.

#### Structure of Films.

The conclusions which may be drawn from films by X-ray method are naturally much more limited than for fibres, but it may be asked first of all whether work on films has provided any evidence of the solvated single molecule as the solution unit rather than the micelle.

In his examination of nitrocellulose films Trillat 32 found that for 12.95 per cent. nitrogen or over, the film showed crystalline characteristics, and gave in particular an intense ring corresponding to the most intense diffraction spot on the equatorial line of the fibre diagram. For less than this amount of nitrogen the films appeared to be almost amorphous. Now on a fibre diagram of nitrocellulose of say 12.2 per cent. nitrogen this spot is strong and is almost as sharp as on the diagram of the trinitrate. If the micelle is the solution unit it is difficult to see why it should be preserved in the film of the more nitrated product (Nitrocellulose I, to adopt Hess and Trogus notation) and lost in that of the other. If. however, the chain molecule is the unit the reason for the failure of nitrocellulose II to recrystallise in the film is the same as for the comparative lack of structural perfection in the fibre, and the most ready explanation is found in the effect of the varying nitration, which at the critical point of 12.8 per cent. produces a chain molecule which is capable of sufficient lateral adherence to crystallise more completely and readily from solution than a less nitrated one.

This difference in nitrocellulose films is independent of the complications which may be caused by the presence of residual solvent, for an examination of numerous films from which all but a minute amount of acetone has been removed by a method of long soaking in water at 45° C. has shown the same results as those already noted (†). The crystalline character of a film prepared from nitroramie of more than 13 per cent. of nitrogen is shown by the presence of no less than five diffraction bands.

The solvent retained by a film may be much greater than is usually suspected. By evaporation of an acetone solution Trillat <sup>24</sup> obtained a film of 12.95 per cent. nitrogen which gave an inner ring corresponding to a spacing of 9.3 Å. He thought that this represented a new variety of nitrocellulose, although admitting the possibility that a combination with the solvent might explain the difference. In an extension of this work <sup>33</sup> the second explanation has been accepted as the true one. Similar experiments (†) made with both nitroramie and nitrocotton have confirmed this conclusion. The films contained, even after long drying, from 3-4 per cent. of solvent, but when this was removed by the process mentioned and X-ray diagrams were made with a canal of the dimensions used by Trillat the spacing of 9.3 Å no longer appeared.

In a recent note Desmaroux and Mathieu <sup>34</sup> report their results with films of nitrocellulose (13·13 per cent.) made from acetone solutions of different concentrations. The more concentrated the solution the more crystalline was the film. This is an interesting result. Their interpretation is that the dispersion in the more concentrated solution is less perfect, the elementary fibres formed of chains of glucose residues being less completely separated from each other.

<sup>32</sup> J. Physique et Radium (7), 2, 65, 1931. 33 Trillat Comptes Rendus, 194, 1922, 1932. 34 Comptes rendus, 194, 2053, 1932. † See note on p. 115.

The applications of the methods of electron diffraction to films of celluloid and nitrocellulose much thinner than those used for X-ray work have given results which seem to point to a greater facility of crystallisation when the film is thin; Dauviller 35 found in one of his films of nitrocellulose an area 0·1 mm. wide which gave a point diagram with hexagonal symmetry. Taylor Jones 36 has obtained similar reresults, and there is no doubt that the second, less crystallisable nitrocellulose, may have this increased facility of arrangement, for the result is the same whether celluloid or nitrocotton of 12·2 per cent. is employed. 37

#### Conclusion.

The formation and structural properties of the nitrocelluloses, with the possible exceptions of those containing less than about 7.5 per cent. or more than 12.8 per cent. of nitrogen, can be accounted for by a consideration of the effect on the long chain-molecule of the intramicellar processes which go on in the structure during nitration. Nitrations of the first class (to less than 7.5 per cent.) may be explained, on the basis of the X-ray results, as heterogeneous reactions taking place at the internal surface, but in view of the ease with which nitric acid penetrates the cellulose structure it is equally likely that these reactions also are intramicellar. Nitration in the intermediate zone (7.5-10.5 per cent. nitrogen) is accompanied, in all normal instances, by disintegration of the fibre and by high absorption of nitric acid from the nitrating mixture. These phenomena, and others connected with nitration, can be regarded as effects of variation of the degree to which the single chain has been nitrated. The hypothesis which best fits the data is that all the chain-molecules are nitrated to very approximately the same extent, in such a way that the chance of any one being completely nitrated to trinitrate before the rest, is very small. The facts of nitration, the results of the X-ray examination of fibres and films and the phenomena of solution, fit in with this conception. The micellar theory of nitration, according to which a nitrocellulose consists of micelles of cellulose each nitrated to trinitrate in a peripheral layer is not in accord with the evidence.

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The Nobel Laboratories, Ardeer.

 <sup>35</sup> Comptes rendus, 191, 708, 1930.
 36 Phil. Mag., 12, 641, 1931.
 37 Taylor Jones, Induction Coil Theory and Applications, London, p. 241, 1932.

## STRUCTURAL VARIATIONS IN THE NITRO-CELLULOSES.

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The investigations described in the present paper fall under two main heads:—

I. The structural changes revealed by X-ray analysis which accom-

pany variations in nitrogen content of the nitrocelluloses; and

2. The structure of nitrocellulose films obtained by the evaporation of acetone solutions on a glass plate. It is shown how this structure depends on (a) the nitrogen content of the nitrated cotton in solution, (b) the concentration of the solution, (c) whether or not the nitrated cotton has been submitted to treatment in an autoclave, and (d) the temperature of drying.

## I. The Structure of Nitrocellulose Fibres.

The raw material used in these experiments was cotton, from which were prepared nitrocelluloses of nitrogen content varying from 13.9 to 11 per cent. by the methods usually employed in the guncotton industry. The cotton was soaked for one hour at 30° C. in a mixture of sulphuric and nitric acids containing 22 per cent. of nitric acid and diluted with water according to the nitrogen content required; under these conditions the reaction proceeds readily. The nitrated cottons were stabilised by boiling with distilled water for 40 hours. Cotton nitrated at 13.9 per cent. of nitrogen was obtained by continuing in the presence of phosphoric anhydride the nitration already brought about in the sulphuric-nitric mixture, after which it was stabilised by washing with alcohol.

The nitrated cottons so obtained were then examined by X-ray analysis, using the "powder method" of Debye and Scherrer. The radiation employed was the  $K\alpha$  of copper ( $\lambda = 1.54$  Å), the incident

beam being defined by a slit of 0.4 mm. diameter.

The X-ray photographs show the following characteristics:-

(a) They have all in common a sharp ring of diameter corresponding to a well-defined "spacing" lying between 6.6 and 7.5 Å. This dimension increases regularly from the least value corresponding to the lowest nitration to that corresponding to the highest nitration according to the table on the next page. For the purpose of simplifying the argument, we shall denote this ring of small diameter by the letter S.

The results given above agree with those published by Miles and Craik,<sup>1</sup> who worked with nitrated ramie. Their diagrams are more precise than those described here, because they are "fibre photographs;" but we have chosen to work with cotton instead of ramie, in order to

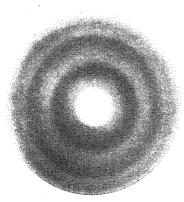


Fig. 1.—Cotton nitrated to 13·39 per cent. nitrogen content.

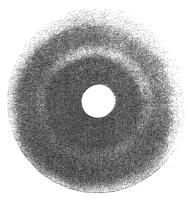


Fig. 2.—Cotton nitrated to 11 per cent. nitrogen content.

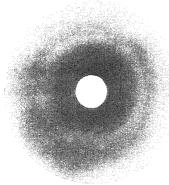


Fig. 3.—Film obtained from cotton nitrated to 13:39 per cent. nitrogen content (very weak solution, decanted).

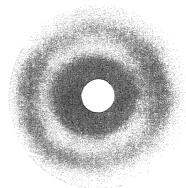


Fig. 4.—Film obtained from cotton nitrated to if per cent. nitrogen content (very weak solution, decanted).

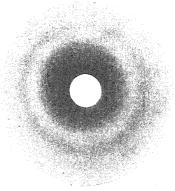
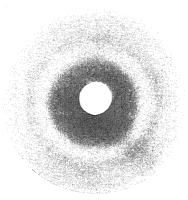


Fig. 5.—Film obtained from cotton nitrated to 13.39 per cent. nitrogen content. (very viscous solution, not decanted).



 $F_{\text{IG. 6.}}\text{--}Film \ obtained \ from \ cotton \ nitrated \ to \ 13\cdot39 \ per \ cent. \ nitrogen \ content, \\ but \ not \ submitted \ to \ autoclave \ treatment.$ 

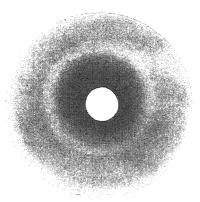


Fig. 7.—Film obtained from cotton nitrated to 13·39 per cent. nitrogen content, but not submitted to autoclave treatment.

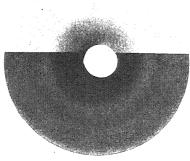


Fig. 8.—Film obtained from a 30 per cent. solution evaporated at 70° C, for five days. (The photograph has been divided into two halves by an aluminium screen.)

[See page 129.

Percentage of Nitrogen.	2 tan 2θ.	Spacing $(d)$ .				
13.9 13.4 12.10 11.7 11.55 11.35	0·41 0·42 0·43 0·435 0·4575 0·465	7·5 7·3 7·2 7·1 6·7 6·6				

be able to apply more easily observations made on fibrous nitrocellulose to the case of amorphous films. To obtain a clear idea of the degree of nitration dealt with in these experiments, it may be recalled that the nitrocellulose of composition  $C_6H_7O_2(NO_3)_3$ , (M=297), has a nitrogen content of 14.14 per cent., while dinitrocellulose corresponds to a nitrogen content of II.II per cent.

(b) Trinitrocellulose (cotton with 13.9 per cent. nitrogen content) shows two sharp, intense rings, as clear as the ring described in the preceding paragraph. These two rings correspond to angles defined by

2 tan 
$$2\theta = 0.70$$
,  
2 tan  $2\theta = 0.88$ ,

and

which give spacings of 4.5 Å and 4 Å, respectively. We shall denote these rings by the letters FS. In the photographs of cotton of nitrogen content below 13.9 per cent. these two rings become broad and of diminished intensity. These characteristics become more and more pronounced as the nitrogen content falls, so that even at 12·10 per cent. it is no longer possible to distinguish two rings, but only two uniform, concentric regions which touch, and of which the outer is clearer than the inner.

The photographs shown in Figs. I and 2 are those given by cottons of nitrogen content 13.9 and 11 per cent., respectively. It should be noticed that while the ring, S, of small diameter is independent of nitrogen content, the rings, FS, of large diameter manifest a considerable change. Photographs of nitrocelluloses of intermediate nitrogen content show features intermediate between the two extremes represented by Figs. I and 2.

It should be mentioned that we have made a point of testing the homogeneity of our products by examination under the polarising microscope, following the methods of Chardonnet and Tissot 2 described by Hess,3 at least, as far as that is possible when working with cotton fibres. Preparations which under the polarising microscope appear heterogeneous, that is, which show on the surface colours verging on those of trinitrocellulose but in the interior colours which indicate a lower degree of nitration, give mixed X-ray diagrams in which can be distinguished more or less readily two clear rings and a halo. It may be added that we have often made use of X-ray photographs in order to test the homogeneity of nitration of a specimen of nitrocellulose of which we knew the nitrogen content. The method is particularly convenient in the case of preparations of low nitrogen content.

The changes in the X-ray photograph of nitrocellulose described above must be interpreted as arising from changes in structure, changes

Tissot, Mem. des Poudres, 22, 31, 1926.
 K. Hess, Chemie der Zellulose, Leipzig, p. 360, 1928.

brought about by the variation in nitrogen content. It therefore seems interesting to compare them with those obtained by Müller from the long-chain paraffins, 4 and with those described by Hoffmann and Frenzel 5 by which they were able to follow the swelling of graphitic acid and graphite. It is clear that X-ray diagrams, without any recourse to crystallographic examination, give direct indications of structural anisotropy. Müller's photographs show directly that different planes behave quite differently with respect to temperature variations. Similarly, the photographs of nitro-cellulose discussed here reveal an obvious structural anisotropy with respect to the introduction of nitrate groups into the cellulose molecule. We shall now go further into the interpretation of these photographs and seek to determine which structural elements are independent of nitrogen content and which are affected by alterations in the degree of nitration.

We may compare the photograph of nitrocellulose of 13.9 per cent. nitrogen with that given by ramie at the maximum possible degree of nitration, when it is seen that the inner ring of the powder diagram of nitro-cotton corresponds to the intense, equatorial spots which are nearest the centre of the fibre diagram of nitro-ramie. These spots are those called  $A_1$  by Herzog and Naray-Szabo  $^6$  and  $B_1^{\circ}$  by Naray-Szabo and v. Susich. They evidently arise from planes not involving the period along the fibre axis, and of the form (hol), b being the crystallographic direction parallel to the fibre axis. It is this family of planes of which the distribution still remains strictly periodic when the nitrogen content varies. It should be observed that this regularity of the planes (hol), which do not involve the period along the fibre axis, is also shown by the photographs published by Miles and Craik. In these photographs, which are "fibre diagrams," it can be seen that all the planes of the zone of which the zone-axis is the fibre axis still give sharp spots, while all the other planes (hkl) give spots of which the sharpness is enormously affected by a decrease in nitrogen content. In the powder diagrams of nitro-cotton it is possible to observe only the (hol) plane of spacing round about 7 Å. (This plane is probably (101); the reflections from other planes of the zone [010] are masked by more intense reflections from other zones. One can easily see from the photographs of Miles and Craik how this comes about.)

To summarise, from this preliminary examination of nitro-celluloses in the fibrous state, we may conclude that decrease of nitrogen content has no effect on the regularity of distribution of planes in the zone about the fibre axis ((hol) planes), while all other planes ((hkl) planes), that is, those which involve the period along the fibre axis, show a regularity of distribution that is considerably diminished. There are, in addition, small variations in the "spacings."

If we assume that the nitration of cellulose is a topochemical reaction which takes place in the body of the crystalline structure, such as has been discussed by Meyer and Mark, we are thus led to the conclusion that the nitrate groups are introduced in an irregular fashion down the sides of the chains of glucose residues; the latter remain at a constant distance apart in the chain, but complete regularity is restored only as the composition approaches that of trinitrocellulose, that is to say, only when all the hydroxylgroups have reacted.

A. Müller, Proc. Roy. Soc., 127A, 417, 1930.
 U. Hoffmann and Frenzel, Ber., 63, 1248, 1930.
 Herzog and Naray-Szabo, Z. physikal. Chem., 130, 616, 1927.
 Naray-Szabo and v. Susich, Z. physikal. Chem., 134, 264, 1928.

## II. The Structure of Nitrocellulose Films.

## (a) The Effect of Nitrogen Content.

Acetone solutions were made from the nitrated cottons of which the X-ray diagrams are described in Section I. These solutions were poured on to glass plates and left to dry, at ordinary temperature, in a desiccator containing sulphuric acid. Acetone was chosen in preference to other solvents because it dissolves all nitrocelluloses, even those of high nitrogen content. X-ray photographs were taken of the films so obtained, the film thickness being always about the same, that is, about three or four tenths of a millimetre. The incident beam was defined by a slit 0.6 mm. in diameter: a slit of 0.4 mm. diameter, such as was used for the photographs of the nitrated fibres, made the time of exposure too long, without sensibly increasing the definition.

The X-ray diagrams of the films show the following characteristics. In every case, whatever the nitrogen content, there is a halo of large diameter which is too diffuse to permit exact measurements of the position of maximum intensity. But it can be seen that this halo occupies the same region as the broad zones or outer rings denoted in the photographs of the nitrated fibres by the letters FS: if  $\theta$  is the "glancing

angle," then

$$0.68 < 2 \tan 2\theta < 0.90$$
.

In what follows we shall denote this halo of the X-ray diagrams of the amorphous films by the letters FSA. The edges of the halo grow gradually clearer as the nitrogen content is increased.

There is also a halo which corresponds to scattering at small angles and which is located round the central spot. This central halo is the part of the diagram which changes most with variations of the nitrogen content. At low percentages of nitrogen it is faint and extends from the central spot, while gradually becoming weaker, to vanish in the neighbourhood of the first sharp ring which we called S, and for which

2 tan 
$$2\theta \approx 0.43$$
.

When the nitrogen content is increased, this halo, which we shall call SA, grows stronger, and at the same time its outer edge becomes more and more sharp. For cottons of very low nitrogen content (II per cent.) it is weak, but for cottons containing from 12·34 to 13 per cent. it forms on the photographs a large black spot with clear, and even dense, edges. Similar remarks apply to the photographs of nitrocellulose films published by Trillat.<sup>8</sup> The relation between the diagram given by films of high nitrogen content and that given by films of low nitrogen content is shown clearly by the photographs of Figs. 3 and 4.

It will be convenient to insert here a few observations regarding the preparation of the films from the photographs of which we have been able to draw these comparisons. Cottons of 12·10 per cent. nitrogen content and lower give films of which the X-ray photographs can always be reproduced; but this is not true for higher nitrogen contents. For example, two films made apparently under the same conditions from cotton of 13·3 per cent. nitrogen content gave different diagrams; one showed the features described above, while the other gave a diagram recalling that of the original fibres. In this latter diagram the outer halo FSA is split into two clear rings quite like the rings FS of the fibre diagram, while the central halo SA ends so sharply as to recall even

<sup>&</sup>lt;sup>8</sup> J. J. Trillat, J. Physique, 7th series, 2, 65, 1930.

more strikingly the ring S of the fibre diagram. (These differences can be seen from the photographs of Figs. 3 and 5.) With cottons of nitrogen content higher than 12.34 per cent. regular variations in the X-ray photographs can be observed only if the solutions have been made very weak and allowed to stand for three weeks before decantation. Unless these precautions are taken, the diagram of the film shows a greater or less resemblance to that of the original nitrated cotton, at least with respect to the splitting of the halo FSA into rings. It should be mentioned that in every case the homogeneity of the films was tested with the aid of the polarising microscope.

What is clear from an examination of the photographs of nitrocellulose films is the analogy which exists between them and those of the original nitrocellulose. The edge of the central halo SA always corresponds to the sharp ring S which arises from a plane of the form (hol), and the rings or zones FS of the fibre diagrams merge into the halo FSA. We have seen that these rings arise from planes of the nitrocellulose lattice which involve the period along the fibre axis (planes of the form (hkl)). In the film, therefore, there still remains something of the regularity which formed the basis of the original structure of the fibres. Furthermore, in the passage from the fibrous state to that of the amorphous film we see a new manifestation of the structural anisotropy pointed out in Section I: the periodicity, 4.45 Å, of the planes (hkl) which involve the parameter along the fibre axis, remains, in brief, little affected (the halo FSA is little different from the zones or rings FS); and we have already remarked on the precautions necessary with nitrocelluloses of nitrogen content higher than 12 per cent. in order to be sure of obtaining diagrams which are not those of the original fibres. On the other hand, the regularity of the plane of the form (hol), a plane belonging to the zone about the fibre axis, is quite undermined on passage to the amorphous film.

The central halo can be considered as arising from scattering from chains of glucose residues which are no longer at a constant distance from one another. This distance has a minimum, however, which is the distance which separates the chains in the crystalline state. This conclusion follows from the fact that the halo has a sharp edge corresponding to the S ring of the crystal photograph. A similar interpretation serves to explain the small variations observed in the sharpness of the halo FSA.

It should be noticed that the evolution of the film photograph with variation of nitrogen content is in perfect agreement with the well-known observation that acetone is a better solvent for cottons of nitrogen content below 12.30 per cent. than for those which approximate to trinitrocellulose.

With a view to a further control of the above results, X-ray photographs were taken of acetone solutions of the various nitro-celluloses studied. Different concentrations were examined, up to the maximum it was possible to obtain (30 per cent.). A drop of liquid was enclosed in a hole in a plate by means of two very thin pieces of mica cemented with a cement insoluble in acetone: the thickness of the drop was thus about three or four tenths of a millimetre. All the acetone solutions, whatever the concentration or the type of nitrocellulose dissolved, gave the same photograph, that of acetone. In particular, nothing is left of the ring, S, of small diameter, the great importance of which we have seen in the crystalline nitrocelluloses. This small ring, which depends on the distance between the chains, is completely wiped out, though, as has been shown above, some trace returns when the solvent is evaporated to form

the amorphous film. With regard to the halo of large diameter, observations are difficult on account of the fact that the halo of pure acetone

occupies almost the same place.

In the above examination of acetone solutions we meet again the "swelling" effects which have already been many times investigated, and which result in a disappearance of the X-ray photograph because of a breakdown of the regularity of structure. On drying, regularities return, but in the case of nitrocellulose the process of recovery is too incomplete to produce the precision of the original arrangement of chains. Nevertheless, the X-ray photographs do definitely reveal a tendency to return to the original state, that is, to a regular regrouping of the elementary chains.

We have already emphasised the precautions which must be taken in order always to produce identical films from cottons of nitrogen content higher than 12 per cent., and it has been shown that the differences which appear in the X-ray photographs if the film has not been prepared by the decantation of a very weak solution can be explained on the assumption that its structure resembles that of the original nitrated fibres. It seemed interesting to investigate what factors controlled the variations in the photographs. For this purpose, use was made of a cotton of 13·39 per cent. nitrogen content, a highly nitrated cotton which is easily made in large quantities. (It is always advisable at the outset of such a research to have a sufficient quantity of raw material, so as to be sure always to be working on the same substance.) In the first place, an examination was made of the effect on the structure of the film of (I) the original concentration of the acetone solution, and (2) treatment in the autoclave of the nitrated cotton before solution.

## (b) The Effect of Concentration.

Two solutions were made of nitro-cotton which had not passed through the autoclave; one contained 0.5 gm. of nitrocellulose and the other 4.8 gm. per 100 c.c. Beyond this concentration the viscosity is so high as to prevent effective mixing by shaking, and homogeneity is not assured. From nitro-cotton which had passed through the autoclave solutions were made containing 0.5 gm., 4.8 gm., and 24 gm. of nitrocellulose per 100 c.c. of acetone. As in the experiments described above, the films were dried at ordinary temperature in a desiccator over sulphuric acid. From the X-ray photographs obtained, the following observations may be made:—

In both cases, of cotton which had passed and cotton which had not passed through the autoclave, the diagram approximates more and more to that of an amorphous body as the solution is made weaker; on the other hand, when the solution is more concentrated, it approaches more the photograph of crystalline nitrocellulose. The crystallinity of the product under examination is revealed by the more complete separation of the halo FSA into two sharp rings, and the sharpening of the edge of the central halo, SA. The effect is readily seen in the photographs of Figs. 3 and 5.

Thus we see here the condition that must be observed in order to prepare from highly nitrated cotton, films of which the structure is no longer that of the original crystalline substance. We have examined also the effect of shaking and centrifuging the solutions. Part of each solution was centrifuged (twenty minutes at about 1200 revolutions per minute) after a preliminary shaking, and for each concentration three

films were made, (I) with the solution shaken but not centrifuged, (2) with the upper layers of the centrifuged tubes, and (3) with the lower layers of the same tubes. All three types of film showed an identical structure. The solutions were therefore reasonably homogeneous.

When we consider all the observations so far described on the structure of nitrocellulose films, it would appear that the most important phenomenon involved in the act of solution is the disappearance of the S ring of the X-ray photographs, that is to say, the disappearance of all regularity of distribution in the plane of form (hol) which contains the elementary fibres built from chains of glucose residues. The solvent has separated these filaments by swelling, and has dispersed them into solution. A regrouping of the chains of glucose residues tends to take place, but it is clear that this tendency becomes less and less as the cotton grows "more soluble" in the acetone. Furthermore, we have just shown that with a cotton of given nitrogen content the tendency for the chains to regroup themselves becomes more and more pronounced as the solution becomes more concentrated. Both phenomena are described by the general statement that the more soluble is the nitrated cotton the more the solvent disperses it into solution, and the weaker the solution the more the cellulose substance is dispersed too. This concept of the dispersion of the nitrocellulose becomes important when we remember that the X-ray photograph of the film obtained by evaporating the solution can reveal the state of dispersion of the cellulose substance.

Hitherto, the only property which has given any indications of the state of dispersion of matter in solution has been viscosity: but it is a very complex property, and we have no assurance that it depends even

on the separation of the chains of glucose residues!

From this idea, that in solution the molecular chains are separated, we can correlate two observations made in quite different fields. The molecular weight of cellulose determined from measurements of osmotic pressure is always of the order of from 30,000 to 40,000. If then our idea is sound that in solution the molecular chains play the rôle of separate particles, the molecular weight should correspond to that of a chain of glucose residues. It is therefore very significant that Haworth, by purely chemical methods, has been able to show that the number of glucose residues in an elementary chain is of the order of 200, from which the weight of a chain must be of the order of from 30,000 to 40,000.

Finally, from the above concept of dispersion, we see that the solvent first acts as a swelling agent, and then plays a similar rôle with regard to the structure of nitrocellulose, as heat does with regard to the structure of crystals near the melting-point. There is indeed a striking analogy between the structure of nitrocellulose and that of the paraffins. On the one hand, the S ring gives place to the central halo on passage into solution, and this change takes place abruptly; on the other hand, the FS rings retain their characteristics more or less unchanged. These phenomena are quite analogous to those described by Müller 4 for the melting of the paraffins.

## (c) The Effect of Autoclave Treatment.

We shall now proceed to a comparison of films made from nitro-cotton which had not been submitted to autoclave treatment, with those made

from the same nitro-cotton heated under pressure in distilled water at  $130^{\circ}$  for twelve hours. We shall denote the former films by the letters fC, and the latter by the letters fCA. If we compare two films made from these two types of nitro-cotton, dissolved at the same concentration, we see that an fC film has always a more pronounced crystallinity than an fCA film (see Figs. 6 and 7).

The lower degree of crystallinity does not show itself, as in the case of dilution, by a loss of sharpness in the edge of the central halo, but solely by a fading of the two FSA rings, which merge into a large halo analogous to that always observed with films prepared from cotton of low nitrogen content. It has been pointed out in Section I that the nitrogen content of nitrocellulose in the fibrous state affects the definition of the FS rings; but the phenomenon seems to be different from that observed with cottons passed through the autoclave, since the rings are not affected in the same manner in the two cases. In the first case, the FS rings spread out into uniform zones, the intensity of which tends to become more and more equal as the nitrogen content falls; while in the second case, the FS rings are always perceptible in the halo, exactly as if we are dealing with a broadening and weakening of the reflected rays from some such cause as a diminution in the size of crystalline particles. It therefore seems reasonable to relate the loss of crystallinity of the fCA films with respect to the fC films to a shortening of the diffracting elements caused by the passage of the nitro-cotton through the autoclave. The action of the autoclave would then be to cut the elementary chains of glucose residues. Such a process would explain well the enormous fall in viscosity of solutions passed through the autoclave, without having recourse to other hypotheses, such as that of the existence in nitrocellulose of a degradation product different from nitrocellulose. The viscosity would then be a property of the free chains in solution, as postulated above, chains of which the length may be variable.

We have, however, to envisage the possibility of the formation of a new substance, and so to test this, photographs were taken of the nitrocotton after autoclave treatment, but before solution. The photograph of the nitro-cotton does not change, whatever the time of treatment in the autoclave. This conclusion was arrived at after experiments in which the nitro-cotton was left in the autoclave for twenty-four hours. There is never any indication in the photographs of the solid residue of the presence of a new crystalline substance other than nitrocellulose. Autoclave treatment always brings about a certain loss in nitrogen content, but this change is too insignificant to give rise to any serious alteration of the photograph.

The same phenomena have been observed with "poudre à canon." If a thin layer of powder of pure nitrocellulose is heated at 110° C., a similar change takes place to that produced by the autoclave. The X-ray photograph of the powder is not modified by the heat treatment. (This photograph shows how well the material is oriented by passage through the press.) But if the nitrocellulose is dispersed by solution in acetone and then evaporated on a glass plate, the photograph of the film made by dissolving unheated powder is sharper than that given by the film from the heated powder.

The question thus arises of how to reconcile the facts that the film photograph indicates shorter particles, while the photograph of the crystalline substance shows no change. Without becoming too hypothetical, we might suppose that the diffracting elements lying along the

fibre axis are indeed cut by the action of heat, but that they remain sufficiently well in position not to disturb the regularity. It would seem that the dispersion of the molecular chains in solution is necessary before the effect of heat is revealed by X-ray photographs. Such a mechanism would also explain the well-known fact that films prepared from autoclave-treated nitro-cotton are much more fragile than films prepared from the normal fibres.

## (d) The Effect of Temperature.

When all the results of the investigations described here are compared with those recently published by Trillat, 10 it would appear that there is a disagreement between the two series of observations. Both series relate to nitrocelluloses of nitrogen content about 13 per cent. Under the working conditions adopted by Trillat, he obtains always films which give rise to X-ray photographs which are very like, if not identical with, those given by the original nitro-cotton. On the other hand, we have always observed a great difference between the photographs of nitrated cotton and those of the corresponding films,—in fact, we have even made use of such differences in order to follow the state of dispersion of the nitrocellulose in solution.

We have now investigated the origin of the discrepancies between the photographs of Trillat and those described above. First films were made at ordinary temperatures in the usual manner from nitro-cotton of 13.3 per cent. nitrogen content. The solutions were 5 per cent. and 30 per cent. (It should be noticed that 5 per cent. is already a strong solution, and therefore of considerable viscosity.) Then fractions of these two solutions were evaporated in a drying-oven at 70° C., in the manner adopted by Trillat, for five days.

The structure of the films is quite different according to the temperature of evaporation. The film dried at 70° C. shows a crystallinity almost equal to that of the original nitro-cotton. In particular, the S ring, which is characteristic of the inter-chain distance of nitro-cottons, reappears,

sharp and intense (see Fig. 8).

If now we compare the photographs of films dried at 70° C., but made from two solutions of different concentrations, we observe the effect of concentration. This effect acts always in the same way as in the case of films prepared at ordinary temperatures: the two FS rings are more obvious when the solution is a 30 per cent. one. Furthermore, the S

ring is also more intense.

Thus at the same time we are able to explain the differences between the photographs of Trillat and those described here, and also to bring out the effect of the temperature of drying on the structure of nitrocellulose films. By drying at 70° C., the X-ray diagrams reveal once more the periodicity due to the lateral separation of the molecular chains of glucose residues. From this we may conclude that heat facilitates the natural tendency of the chains to dispose themselves in a regular manner, that is, a kind of annealing takes place. A similar phenomenon has already been observed in the case of films made from nitrocellulose and benzophenone, or nitrocellulose and methyl-naphthyl-ketone. 11 It is difficult, however, to state definitely that we are dealing with an annealing process analogous to that which takes place in metals. It would be necessary

<sup>10</sup> J. J. Trillat, C.R., 1932 (in proof). <sup>11</sup> Desmaroux and Mathieu, C.R., 191, 786, 1930.

to trace the curves showing the loss of solvent with time at any given temperature, and to follow simultaneously the structural changes by means of X-rays. Up to the present, we have been able only to touch upon this question of the effect of temperature, but it is hoped to go into the matter later in more detail. It has been thought worth while, however, to report the present results, incomplete as they are, on account of the special interest of the questions involved.

## Summary.

r. It has been shown how the structure of the nitrocelluloses in the fibrous state changes with the degree of nitration. On the one hand, the elementary chains of glucose residues remain separated at well-defined distances, which, however, vary slightly with the nitrogen content; on the other hand, it would appear that the nitrate groups are distributed at random along the chains. Strict regularity tends to reappear as the composition of trinitrocellulose is approached.

2. From a study of the different factors which determine the structure of nitrocellulose films, it can be said that the solvent acts first as a swelling agent and afterwards as a dispersing agent: under its action the molecular chains are dispersed. From the X-ray photographs of films obtained by drying, it is possible to follow the state of dispersion in solution. This dispersion is the greater according as the nitrated cotton is more soluble in the solvent. With a given nitrocellulose, it increases with increase of

dilution

The action of the autoclave on the nitrocelluloses is that of a fractionation of the elementary chains of glucose residues. The viscosity of a solution of given concentration depends on the length of the linear elements which constitute the chains.

Finally, drying at a higher temperature than the ordinary brings about in the structure of the film a more regular regrouping of the chains, that is to say, induces a kind of recrystallisation of the cellulose substance.

The above investigations have been carried out partly at the Laboratoire Central de Poudres, and partly at the Laboratoire de Chimie Générale of the Sorbonne. All the products have been prepared under the supervision of Monsieur Desmaroux, Director of the Powder Laboratory.

In conclusion, I wish to thank Professor Urbain for his continual encouragement and valuable criticisms.

Paris. 7th August, 1932.

#### GENERAL DISCUSSION.

Mr. W. T. Astbury (Leeds) said, with regard to M. Mathieu's paper: The X-ray evidence for the mechanism postulated by M. Mathieu for the substitution of the nitrate groups in the cellulose chain is strictly analogous to that which reveals the attack of steam on the side-chains of the main protein chains of the keratin of wool and hair. This unidirectional change is a comparatively rare phenomenon in structure analyses. In nitrocellulose, according to Mathieu, all planes are affected by the process of nitration except those which have the cellulose chain axis as zone-axis, while in keratin only those planes remain unaffected by the action of steam which have the side-chain direction as zone-axis.

**Dr. J. R. Katz** (Amsterdam) said: There now exists good X-ray evidence that camphor can form one or more chemical compounds with nitrocellulose. J. C. Derksen and I, in collaboration with Kurt Hess and Carl Trogus in Berlin, found that both in celluloid and in fibres swollen in solutions of camphor, new X-ray diagrams occur, different from the diagram of nitrocellulose, which must be explained as diagrams of compounds.

Most of the synthetic substances used as substitutes for camphor in celluloid (such as diphenyldiethylurea, ethylacetanilide, alkylphthalates, cyclohexanone, toluenesulphamide, etc.) give changes in the X-ray diagram (both of fibres and of celluloid), which point to the existence of chemical compounds between these substances and nitrocellulose. Solvents of nitrocellulose, too, can often give such compounds with nitrocellulose.<sup>1</sup>

Very often the substances which can give such compounds contain the group C=O (which, however, can be substituted by P=O or by  $SO_2$ ). It is probable that these are not compounds formed by chief valencies, but are of the character of "molecular compounds" (Moleküle verbindungen) in the sense of P. Pfeiffer.

<sup>1</sup> Z. physik. Chem. 149A, 371, 1930; 151, 145, 163, 172, 1930; 7B, 17, 1930.

# PROTEIN STRUCTURE AND PROTEIN HYDRATION.

By Dorothy Jordan Lloyd and Henry Phillips

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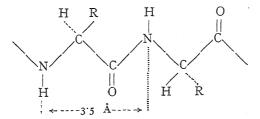
(From the Laboratories of the British Leather Manufacturers' Research Association.)

#### Protein Structure.

The early workers in protein chemistry devoted almost the whole of their attention to the problem of isolating and determining the constitution of the structural units of the different proteins. Although Fischer and other workers produced evidence that the units were mainly joined through peptide linkages, the problem of the structure of the protein molecule as a whole has remained obscure up to the last few years. The use of X-rays for examining the atomic structure of solids has, however, opened up a new line of attack on this subject and the work of Brill (1923), of Katz and Gerngross (1926), Meyer and Mark (1928) Astbury (1930) and Speakman (1931), on the X-ray examination of fibrous proteins starts a new chapter in protein chemistry. A lucid review of the present position as regards the fibrous proteins has recently been given by Astbury (1931).

Silk, stretched hair or wool and collagen fibres have been shown to be built up of long chain molecules lying parallel to the fibre axis. The long molecules consist of a repeating unit, of which three atoms lie on the spiral or zig-zag axis of the molecule, while the remainder form lateral extensions—the whole being a long polypeptide chain with the length of

the repeating unit 3.5 Å.U. Diagrammatically, the molecule in its simplest form with zig-zag axis may be represented as:—

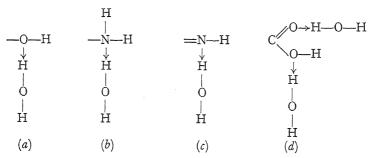


Evidence has been given elsewhere (Jordan Lloyd, 1932) that as long as the chain is in the simple untwisted form the N, C, C atoms of the main axis together with the hydrogen atom of the imino group and the oxygen of the ketonic group, may be regarded as lying in the plane of the paper, whereas the hydrogen atom and the R group of the asymmetric carbon atom project above and below the plane respectively. As the spatial configuration of all the amino acids is the same, the orientation of every R group in the protein molecule is fixed in relation to the structural unit. The chemical characteristics of the proteins as a class are determined by the chemical properties of the repeating unit—those of the individual proteins by those of the R groups.

## The Hydration of Proteins.

Proteins are colloids primarily because their molecules are large, but the colloidal properties of all proteins are not the same because the chemical nature of the R groups varies from protein to protein. The colloidal properties of a protein are dependent on the ease and degree with which it becomes hydrated. When many of its R groups contain oxygen and nitrogen atoms, the affinity of the protein for water is greater than is that of a protein of which the R groups are mostly hydrocarbon chains.

The oxygen atoms of protein molecules occur either in carboxyl, amide or hydroxy groups, the nitrogen atoms either in amide, imino or amino groups. In all these groups, both atoms possess electrons which are not utilised in co-valent linkages and may, therefore, co-ordinate with water molecules as indicated.



In addition, the hydrogen atoms of these groups may form co-ordinate links with the unshared electrons of the water molecules.

electric point protein molecules will hold some water. In hydrochloric acid solution, these molecules become polykationic and are associated with mono-valent chlorine anions which have a much smaller affinity for water than the protein ions. For both these reasons, therefore, the protein chloride may hold far larger quantities of water than the protein molecule can hold at its iso-electric point, and for similar reasons sodium salts of proteins would show the same power. In both the anionic and kationic states the protein molecule in solutions of simple acids and bases is, of course, far larger than the ions with which it is associated and this suggests an additional reason for the occurrence of heavy hydration. It must be remembered that in considering the total amount of water which passes into a protein jelly or into a sol enclosed in a membrane, as distinct from the amount directly associated with the protein, the establishment of a Donnan equilibrium due to constraint on the movement of the protein ions will probably be the paramount factor in fixing the equilibrium of the system as a whole. The influence of acid and alkali under these conditions has been discussed on innumerable occasions, (see especially, Bolam, The Donnan Equilibrium, London, 1932).

In the case of protein molecules in contact with an iso-electric solution of an electolyte, entirely different conditions obtain from those present when the solutions are either acid or alkaline. At its iso-electric point each protein molecule possesses anionic and kationic centres and, furthermore, each protein Zwitterion is identical either from the standpoint of its valency, degree of hydration or its size. Such molecules may, however, become orientated with respect to one another under the influence of the oppositely charged centres which they contain, and in this condition can be regarded as salts. The ions of these salts are identical, and for this reason the hydration of the protein as a whole will not be augmented by the forces which cause the chloride and sodium salt of the protein The addition of a simple salt, such as sodium chloride, to the iso-electric solution of the protein should, however, increase hydration because some of the charged centres in the protein molecule would become associated with sodium and chlorine ions. The "mixed" protein salts produced would tend to hydrate like the true salts of the protein.

All the three factors discussed above which affect hydration are intimately connected with the size of the ions. Size and structure also influence the arrangement of the ions in the crystal state and decide the number of water molecules which are required to produce a symmetrical and balanced unit. Similar considerations apply to the hydration of protein molecules. The degree of hydration attained by the protein molecule as a whole will depend on the length and bulk of the side chains or R groups and the extent to which the molecules become closely packed together either by natural or artificial means. Protein molecules with short R groups can approach closer together than those with more elongated R groups. The shorter R groups will, therefore, be expected in dry," compact fibres such as silk or hair, and the longer R groups in "wet" fibres such as collagen fibres. Similarly, the degree of hydration which an organised protein composed of orientated molecules can attain can be increased by destroying the ordered arrangement of the molecules; water can then approach the disorganised molecules more freely and hence hydration proceeds to the maximum extent. Disorganised collagen fibres or gelatin and disorganised silk fibres or fibroin thus hydrate to a higher degree than the organised fibres.

The molecules of an organised protein can approach as closely as the length of their side chains permits. At the iso-electric point, when each molecule of the structure contains anionic and kationic centres, they will tend to be drawn together by electrostatic attraction which will favour the closest degree of packing and hence the lowest degree of hydration. On either side of the iso-electric point each protein molecule contains predominantly either anionic or kationic centres and the molecules mutually repel each other. By this means, the spaces between the molecules in an organised protein are increased, leading to an increase in the amount of water which can enter freely between the individual molecules.

The degree of hydration which a protein can attain may, therefore, be expected to depend (1) on the proportion of hydroxy-amino acid residues and amino- and imino- containing residues which are built into its molecules, and (2) on the number of free amino and carboxyl groups it contains, and (3) on the structural organisation of the molecules, closely packed structures such as fibres being less hydrated than a group of molecules orientated at random. The nature of the linkages between the molecules of an organised protein may also influence the degree of hydration to which it attains. When these linkages are electrovalent and consist solely of the attraction between oppositely charged groups, they are capable of extension and change of direction, and will not prevent the intrusion of water between the protein molecules although they may set a limit to the amount which enters. Speakman and Hirst (1931) have suggested that a lysine-glutamic acid linkage of this type exists in keratin. A disulphide linkage formed between two cysteine R groups in adjacent protein molecules would link them together more firmly, this type of linkage being co-valent and possessing a definite and unalterable length. Before protein molecules linked in this manner could separate a chemical reaction would be necessary to break the disulphide linkage. Marriott (1925) has shown that when the disulphide linkages of keratin are disrupted, this protein becomes more susceptible to the action of acids and alkalies, suggesting that in the absence of the disulphide link it hydrates with greater freedom.

## The Hydration of Tissue Proteins.

It is a generalisation of considerable significance that the percentage of water in any tissue always bears a direct ratio to its biological activity (see Needham, 1932, and Jordan Lloyd, 1932). It becomes, therefore, of interest to examine the proteins from the different tissues and to compare their degrees of hydration. Since this will be influenced by the nature of their side chains, the possible groupings which occur in proteins as R groups will be briefly reviewed.

These may be hydrogen atoms, aliphatic chains of I to 4 carbon atoms in length, or they may be groupings containing a benzene, indole or imidazole ring; amino or guanidine groups; carboxylic groups and acid amides; even sulphydryl or disulphide groups. In some cases, the side chains are hydroxylated, the hydroxyl group being in nearly every case on the  $\beta$ -carbon of the amino acid.

These side chains project from the main axis of the molecule and vary considerably in length. The shortest is the hydrogen atom, which forms a side chain of 1.2 Å.U., while the longest is the indole-methyl grouping contributed by the tryptophane residue, which may be cal-

culated from the results of Lonsdale (1929) to project approximately 12.5 Å.U.

A classification of the side chains according to their affinity for water, as deduced from theoretical considerations, is given in Table I. The

TABLE I.

Amino Acid.	Affinity of Side Chain for Water.	Solubility of Free Acid in g. per 100 c.c. Water. 20-25°.	Approximate Length of Side Chain in Å.U.
Glycine Alanine Valine Aminobutyric Iso-leucine Leucine Norleucine Phenyl alanine Cystine Tyrosine Tryptophane Histidine Aspargine Glutamine Glutaminic acid Aspartic acid β-hydroxyglutaminic acid Proline Hydroxyproline (δ-hydroxy α-amino-valerianic acid) (δ-γ-hydroxy α-amino-valerianic acid) Serine (β-hydroxy alanine) Lysine Arginine β-hydroxylysine β-hydroxylysine β-hydroxylysine β-hydroxy valine β-hydroxy valine	Slight increasing slowly downwards  Pronounced	51 13.87  2.2 at 18°  1.49 0.017 0.045 1.31  1.12 0.67 0.41 5.1 Soluble "  Not known in the free state Soluble Very soluble Soluble " Soluble "	1·2 2·5 3·7 5·0 6·3 2·5 7·5 12·5 6·5 5·1 5·1 3·8 About 4 ,, About 6 ,, About 3·5 7·5 About 8·8
Glucosamine mannose	Very strong	,,	

acids have been arranged in groups on the assumption that saturated aliphatic chains are without affinity for water; that hydroxyl and amino and, to a lesser extent, imino groups, all of which have lone pairs of electrons, are able to co-ordinate with water molecules, and that the affinity of these groups for water will be at a maximum when they occur in open chain compounds, but reduced when they occur in ring compounds and compounds with double bonds, owing to the pull of these structures on the electrons. Besides the theoretical affinities of the R groups for water, Table I. also gives the solubilities of the free amino acids, as far as these are known (Seidel, 1920, 1928). The solubilities of the latter are influenced largely by their amino and carboxyl groups and the extent to which these two groups are separated from each other. The figures, therefore, may give only a rough indication of their behaviour when linked into the polypeptide chain. It is, however, very strikingly shown in the monobasic-monocarboxy acids how increasing the length of the aliphatic chain tends to draw the molecule out of solution and how the presence of a benzene ring also leads to loss of solubility. Although quantitative records are not available for hydroxy acids and basic amino acids, qualitative data are sufficient to show the strong effect of hydroxyl and amino groups in increasing solubility.

Table II. gives five analyses of proteins (representing various degrees of biological activity): (1) from the testicular cells, the cells showing the most active rate of growth and division in the adult body, (2) from muscles, biologically active tissues but not undergoing division in the adult body, (3) from the endo-skeleton (connective tissues), (4) from external structures completely devoid of any biological activity, namely, horse hair, (5) from external secretion of the body, namely, silk fibroin.

Pronounced affinity. R has no affinity for water; Slight affinity, increasing Hydroxy Glutamine, Hydroxy Proline. Glutaminic Acid (or Glutamine). Aspartic Acid (or Asparagine) henylalanine, Tryptophane, Histidine, Tyrosine. Arginine, 3lycine. Alanine, Leucine Cystine Lysine, Salmin 1 7.8 87.4 4.3 11.0 Chicken muscle 2. ? 16.48 ? 0.68 2.58 11.0 2,16 2.47 3'21 7.94 6.5 3.23 4.74 Gelatin 3 8.7 5.8 1'4 0,0 25.5 0,0 7.1 0.0 0.0 0.0 3'4 9.2 14°1 0.0 0.4 2.9 8.5 Horse-hair 4 8.0 1.2 7.I 0,3 0.6 1.1 0.6 7.6 0.0 3,5 3.7 4.7 3'4 Silk fibroin 5 1.8 0.25 40'5 25'0 2.2 11.0 0.7 0.74

TABLE II.

No direct evidence of the hydration of salmin is available, but the presence of an enormously high proportion of R groups with a pronounced affinity for water suggests that it will be highly hydrated. Salmin does not exist in the living cell in the free state but as a salt of nucleic acid. It will, therefore, probably hold a considerable amount of water by electrostatic forces. The evidence as to the extent of hydration of the remaining proteins is considered below.

#### The Hydration of Muscle Proteins.

In Table II. an analysis is given for the muscle proteins of the chicken. The analytical data for muscle proteins of fish, fowl and mammals are all very similar in character. The figures for glutaminic (and aspartic) acid are high and so are the figures for lysine and arginine. Muscle proteins, therefore, may be expected to show maxima of hydration. due to the influence of charged centres, in both acid and alkaline ranges and, unless the behaviour of the molecules is interfered with by orientation, should also show a minimum near the neutral point. Evidence on the swelling of excised muscles from the frog (Jordan Lloyd, 1917) shows that well marked maxima occur at  $p_{\rm H}$  2.2 and 11.8, but that there is a well marked stability zone between  $p_{\rm H}$  5 and 7 or possibly even 8. Muralt and Edsal (1930), however, have shown that the myogen mole-

<sup>&</sup>lt;sup>1</sup> Kossell and Dakin, 1904. <sup>2</sup> Osborne and Heyl, 1908. 3 Dakin, 1920.

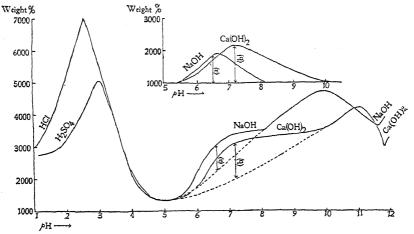
Abderhalden and Wells, 1905; Buchtala, 1907; Argiris, 1907.

Abderhalden, 1922; Vickery and Block, 1931; Vickery and Leavenworth, 1929.

cules are oriented in muscle, and therefore the interpretation is feasible that even under these conditions some of the loci of hydration are suppressed. Of the aliphatic amino acids, the one present in greatest amount is leucine. Parallel orientation of the molecules would not, therefore, lead to very close packing, and indeed muscle is a fairly "wet" tissue containing about 75 per cent. of moisture, but it also is isotonic to about 0 I N sodium chloride and the presence of this salt will lead to a considerable degree of hydration.

## The Hydration of Collagen Fibres and Gelatin.

The collagen fibre is to be regarded as built up of gelatin with its long polypeptide chains arranged parallel and forming a fibre, with electrovalent linkages between the molecules. Conversely, gelatin can be regarded as collagen with its molecules disoriented. An analysis is given in Table II. About one-third of the molecule is built up of the residues of glycine and alanine, the R groups corresponding to which are short (see Table I.) and non-polar with no affinity for water. This will favour close



Curves showing three maxima of hydration of gelatin (1) in acid, (2) in alkali, (3) near absolute neutrality.

packing into a fibre. However, gelatin also contains a large number of R groups with a pronounced affinity for water. These come from the residues of proline (possibly present as δ-hydroxy α-amino valerianic acid) and hydroxyproline and of lysine and arginine. Gelatin and collagen, therefore, may be expected to co-ordinate freely with water at or near absolute neutrality. In addition, gelatin contains side chains which contain polar groups. These are contributed by the aspartic and glutaminic acid residues which form nearly one-tenth of the molecule, and by the lysine and arginine residues which form about one-seventh. Gelatin gels and collagen fibres should, therefore, possess considerable power of absorbing water from acid, alkaline and neutral solutions. This has been shown experimentally to be the case with gelatin gels. The figure shows the curve of swelling of purified leaf gelatin at a range of reactions from 1 to 13 from (Jordan Lloyd and Pleass, 1927; Pleass, 1930). On the acid side of the iso-electric point there is one sharply marked maximum of swelling. On the alkaline side there is a sharply marked maximum at  $p_{\rm H}$  10 and a broad plateau at about 7. Evidence has been given elsewhere that the swelling due to the osmotic effect of the alkaline salts of the gelatin is that with the sharp maximum at  $p_{\mathrm{H}}$  10 and the dotted line shows the amount of swelling to be attributed to this factor at all reactions. The inset figure shows the curve obtained by plotting the difference between the calculated curve of alkaline swelling and the observed figures. It will be seen that this curve has a maximum close to absolute neutrality, and that the height of the maxima are not very different, and are in fact probably the same within the limits of accuracy of the experiment in the presence of sodium or calcium ions. The swelling at the neutral point is to be partly attributed to orientation of water molecules around substituted ammonium and carboxyl ions, produced by salt formation between adjacent amino and carboxyl groups, and partly to co-ordination of water molecules with uncharged hydroxyl and amino groups. Acid swelling is to be attributed to enhanced salt formation at the basic groups of the lysine and arginine radicles with the formation of more numerous and intense positively showing that the charged centres originating in the amino groups play an important part (Kaye and Jordan Lloyd, 1924).

The important feature in the  $p_{\rm H}$ -swelling curve for collagen compared with that for gelatin is, however, the region of stability between  $p_{\rm H}$  4 and  $p_{\rm H}$  8.5 (Jordan Lloyd, 1932). Over this range, the centres of hydration occurring in the collagen molecule are prevented from associating with water by the structural organisation of the fibre. However, even over this range, hydration can be brought about by the action of salts, although the forces leading to hydration show their greatest

effect in the disorganised protein, gelatin.

# The Hydration of Keratin.

The constitution of keratin (horse-hair) is given in Table II. figures must be taken with reserve since less than half the molecule has been accounted for, and recent work has given rather higher figures for the bases in wool (Vickery and Block, 1930), and very considerably higher figures for the glutaminic acid (Speakman and Hirst, 1931). cystine in horse-hair is very high, and may form co-valent cross connections between the molecules or between different parts of the same molecule. In Table III. are given figures showing the progressive hydration of horse-hair in water, acid, alkali and salt solutions. Horse-hair has a slightly increased water absorption which is progressive with time in dilute acid and in dilute alkali and possibly a slight tendency to progressive hydration in the presence of nitrate. It only takes up any considerable amount of water under the action of strong alkali. swelling is also progressive with time and is accompanied by a weakening of the fibre structure similar to that found by Norris (1932) for wool and is not osmotic in character. The polar groups which it undoubtedly possesses by virtue of the dicarboxy and diamino acids built into its structure are placed so that they cannot easily either hold water by electrostatic forces or cause the appearance of a Donnan equilibrium. short, the structure of the fibre prevents the entrance of water. Astbury has postulated a very compact structure of spiral pattern for the keratin molecule in its natural condition. Meunier and Rey (1927) obtained for wool (which had, however, been scoured in alkali and bleached with sulphurous acid, a process which undoubtedly weakens the fibre) a

TABLE III.

Temperature :	~00			Horse-bai	г.		Silk Gut.	
remperature.	= 10	(	ı day.	5 days.	20 days.	I day.	5 days.	20 days.
Water .			128	129	132	132	135	133
N/1000 HCl $N/100$ HCl $N/10$ HCl	:		133 131 126	131 135 137	133 139 147	132 135 127	133 135 130	132
N/1000 NaOH N/100 NaOH N/10 NaOH	:		139 141 207	138 143 286 d	141 151 lissolved	135 131 144	136 136·5 179	136 144 208
M NaCl . 2M NaCl . 2M NaCl at 37°	:	:	132 130 130	133 129 133	135 129 127	132 135 136	 134 136	131 135 136
M NaNO <sub>3</sub> 2M NaNO <sub>3</sub> 2M NaNO <sub>3</sub> at 3	7°	:	134 138 130	135 138 135	142 140 133	136 137 138	137 138	138 136 139

typical protein swelling curve with maxima in acid and alkali— $p_{\rm H}$  1·5 and 7·6 respectively. The acid maximum, like that of collagen fibres, was reduced by deamination.

The keratin fibre is apparently a closely packed fibre, but is not conspicuous for any large amount of very short R groups among its aliphatic amino acid residues. The figures available are not, however, of sufficient accuracy to justify further comment.

## The Hydration of Silk Fibroin and Silk Fibres.

Silk contains two proteins, sericin and fibroin. The former can be extracted from silk fibres by prolonged treatment with hot water. Kodama (1926) has examined the physico-chemical properties of the extracted sericin and finds that it combines with both acid and alkali and shows considerable swelling in hydrochloric acid and in sodium hydroxide. Unfortunately, his experimental figures are not presented in a form which enables them to be compared with the other proteins discussed here and, moreover, no chemical analyses of sericin are available.

Silk fibroin is completely insoluble in hot water, though in common with all fibres it can be dispersed by treatment with hot concentrated solutions of lyophylic salts (von Weimarn, 1928). An analysis of silk fibroin is given in Table II. It can be seen that almost the whole of the molecule is made up of glycine, alanine and tyrosine. The R groups, therefore, in this case will have no affinity for water, the associating properties of the hydroxyl group of the tyrosine being restricted by the electron-absorbing character of the benzene ring to which it is attached. Moreover, Brill (1923) has shown by X-ray analysis that the fibre consists of long polypeptide chains (probably with glycine and alanine alternating) oriented along the fibre axis. The shortness of the side chains (see Table I.) will lead to close packing of the molecules, indeed Kratsky and Kurijama (1931) estimate the side spaces to be between 4·5 and 6 Å.U. In addition, the molecule of silk fibroin contains very

few R groups that could give rise to charged centres. Vickery and Block (1931) have found that lysine and arginine together form only 0.9 per cent. of the molecule. Harris and Johnson (1930) state that "analysis shows that the fibroin molecule contains few free amino or carboxyl groups and that the latter are in excess." An iso-electric point (determined by them from electrophoretic measurements on dissolved and precipitated fibroin) of  $p_{\rm H}$  2.2 is evidence in support of the excess of carboxyl groups, but, unfortunately, no recent analytical figures are available. Denham and Brash (1927), using the combination of threads with coloured positive and negative ions, give a less acid iso-electric point for fibroin, namely, pH 3.8. Harris and Johnson have studied the physicochemical properties of their prepared fibroin and found that it had a certain power of swelling in buffer solutions with a well marked point of minimum swelling at  $p_H$  2. Unfortunately, their results, like Kodama's on sericin, are not given in a form which can be compared with work on other proteins. Silk fibroin, however, when no longer in the fibrous condition, undoubtedly shows a certain degree of hydration. As a fibre, it may be anticipated that it will have little, if any, affinity for water. A few experimental observations confirm this expectation. Silk gut prepared for surgical purposes was used as the experimental material. This is prepared from the silk sac of the silk worm by stretching and maceration. It is a very pure form of silk and has not undergone any commercial "finishing process." Ninety minutes' extraction with boiling water failed to remove any trace of soluble protein and the fibres may, therefore, be regarded as consisting almost, if not entirely, of fibroin. It is a very convenient form of silk for observations on swelling since the fibres are comparatively coarse (average diameter 0.41 mm.) and errors due to surface adsorption are thus reduced to a minimum. The silk absorbs the same amount of water (within the experimental error which is ± 2 per cent.) from distilled water and from solutions of hydrochloric acid; slightly increased amounts from solutions of sodium chloride, from solutions of sodium nitrate and from dilute solutions of sodium hydroxide and rather greater amounts from strong solutions of alkali. The swelling in alkaline solution is progressive with time, and there is little doubt that with silk gut the swelling that occurs with both alkalies and strong salt solutions is only another case of that which occurs with all colloids under these conditions and is not to be attributed to the influence of charged centres originating in amino or carboxylic groups. While, therefore, silk fibroin can co-ordinate with a small amount of water, this is probably largely accounted for by absorption on to internal and external surfaces. Meunier and Rey (1927) give a swelling curve of washed silk threads showing increased swelling in acid and alkali on either side of a minimum at  $p_{\rm H}$  4.2. It is, however, doubtful whether the curve which they show is a curve of pure osmotic swelling since no maxima appear on it. There is, moreover, no evidence as to whether the swelling is progressive with time, and until evidence on this point is available it is difficult to decide how much of the swelling is due to charged centres and how much is due to destruction of the fibre by the strong solutions of acid and alkali. Dr. Denham, however, (personal communication) finds that silk threads show very slight osmotic swelling.

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#### Discussion.

It follows from the evidence reviewed above that the hydration of proteins depends both on the chemical constitution of the protein mole--cules and on the molecular organisation in the material under investigation. A comparison of the amount of water held by 100 parts of dry protein brings this out very clearly. For instance, considering gelatin only, the amount of water held by (undried) gels set at 20, 15, 10 and 5 per cent. original concentration when brought into equilibrium with pure water is 500, 700, 900 and 1600 parts respectively on 100 parts by weight of dry gelatin. For the same four gels, the amount of water over and above this which is absorbed at  $p_{\rm H}$  2.8 is 1900, 2100, .2800 and 4500 parts by weight respectively and for the last three at  $p_{\rm H}$  9.4 is 1300, 1900 and 3100 respectively. This range of variation, which can only be due to differences in structural organisation inside the gels is very great. Even more striking results are obtained by comparing the amount of water held in water and in acid and alkaline solutions for a series of protein structures showing progressively a more fibrous character. These are summarised in Table IV., which shows the parts of water held by 100 parts of dry

TABLE IV.

Parts per 100 Parts of Dry Protein.	Gelatin.	Muscle.	Collagen.	Kera Wool.	Horse- Hair.	Siık Fıbroin (Silk Gut).
Water at minimum swelling	1300	About 300	260	40 <sup>1</sup>	28	32
Additional water held at acid maximum	5200	1100	230	7 ¹	0	0
alkaline swelling	1500	800	120	(if any	tic ma ) lost in aline so	n curve
$p_{\rm H}$ at acid maximum , $p_{\rm H}$ at alkaline osmotic maximum .	2.6	2·3 11·8?	2·I 10·8	1.2	=	_
Lysine	5·9 8·2	7·9 6·5	5°9 8°2	2·3 7·8	1·1 7·6	0·2 0·7
Arginine + lysine	14.1	14.4	14.1	10.1	8.7	0.9
Glutaminic + aspartic acids	9.2	19.7	9•2	15.22	4.0	?

protein material at the point of minimum swelling, at the acid maximum and at the osmotic maximum of alkaline swelling. It is a significant fact that the value of the  $p_{\rm H}$  at maximum acid swelling becomes progressively lower as the structure of the fibre becomes more compact. The  $p_{\rm H}$  at the osmotic maximum of alkaline swelling also becomes further removed from absolute neutrality as the structure of the fibre gets more compact, till, finally, in fibres like wool and horse-hair, it becomes merged with and lost in the curve of swelling in strongly alkaline solutions which is due to the general disruption of the colloid which

<sup>&</sup>lt;sup>1</sup> Meunier and Rey (1927).

<sup>&</sup>lt;sup>2</sup> Speakman and Hirst (1931).

always takes place in such solutions. This effect, *i.e.* loss of a clearly defined osmotic maximum in alkaline swelling, is particularly well shown in the curves of Meunier and Rey for wool, though it is also brought out in those of Kaye and Jordan Lloyd (*loc. cit.*) for collagen (skin) fibres.

If the water held at minimum swelling (frequently called the isoelectric point) is held by forces of co-ordination (donation of lone pairs of electrons), the differences in chemical composition of the protein cannot entirely account for the different amounts held which follow a parallel course to the increasing compactness of the structure. The same is true of water held through the influence of charged centres in the different protein molecules. IV. gives the percentage of diamino and di-carboxylic monoamino acids which have been determined in hydrolysed proteins. The very low amounts of diamino acids found for silk and horse-hair are associated with striking reductions in the acid maxima of these proteins; the comparatively high percentage of di-carboxy acids in muscle is accompanied by an osmotic swelling at the alkaline maximum almost as great as the osmotic swelling at the acid maximum, while the comparatively smaller amount of these acids in gelatin is accompanied by an alkaline maximum much lower than the acid maximum. It is obvious, however, that some other factor besides chemical constitution is influencing the final results. It is suggested that this factor is the organisation of the protein molecules into definitely oriented structures in which cross connections, either by covalent or electro-valent bonds, restrict the power of the protein to hydrate and reduce the space available for water molecules.

#### Summary

I. The hydration of proteins in water is due to the co-ordination of water molecules with the oxygen, nitrogen and hydrogen atoms of the hydroxyl, carboxyl, amino, amido and, to a lesser extent, the imino and keto groups. Water-soluble proteins contain high proportions of the residues of serine or other hydroxy acids, lysine, arginine and proline.

2. At the iso-electric point, protein molecules carrry an equal positive and negative charge. Salt formation, between adjacent protein molecules, and between oppositely charged groups of the same molecule, will not lead to hydration owing to the equal size and valency of the two ions involved.

- 3. In acids and alkalies, the two ions of the protein salt produced differ enormously in valency, size and the readiness with which they hydrate. This leads to increased hydration by the orientation of water molecules around the charged centres in the protein molecule. Acid-soluble proteins contain the residues of lysine, arginine and, to a less extent, histidine. Alkali-soluble proteins contain the residues of aspartic and glutamic acids and, to a less extent, the amides of these acids.
- 4. The hydration of protein molecules in solutions of neutral salts is promoted because the protein molecules become associated with the small ions of the salt.
- 5. If protein ions exist in a system under restraint while other ions are freely diffusible, a Donnan equilibrium will also affect the distribution of the water.
- 6. Solubility and hydration of proteins is greatly affected by the closeness of packing of the molecules into organised structures with cross linkages between the molecules. Cross linkages involving co-valent bonds will be more resistant than those involving electro-valent bonds. Fibrous proteins, particularly those with a preponderance of residues of the short chain aliphatic amino acids are the most resistant to solvents.

7. With the development of oriented structure in proteins, a stability range towards hydrating influences appears. This range extends from

about  $p_{\rm H}$  4 to 8.

8. The  $p_{\rm H}$  value at maximum hydration in acid solutions moves continually to a lower figure as the protein structure becomes more and more fibrous in character. The  $p_{\rm H}$  of maximum osmotic hydration in alkaline solutions becomes greater under the same conditions.

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#### GENERAL DISCUSSION.

Mr. W. T. Astbury (Leeds) said: Since I do not know sufficient about protein structure to dare to disagree with Dr. Jordan Lloyd, I shall take this opportunity of agreeing heartily with the main conclusions of her paper with Dr. Phillips. I should like to say that X-ray studies of the structure of keratin show conclusively that both the association with, and the attack on, protein chains of water molecules takes place

chiefly on that side of the main chains where the side-chains are located. The keratin complex, of which the main chains must be bridged both by electro-valent and co-valent links, affords also a striking example of the influence of organised structure on hydration. Though plenty of active side-chains are revealed by hydrolysis, these are too occupied in holding together the original structure to permit the degree of hydration that might otherwise be expected. One of the functions of these active sidechains, as I have indicated elsewhere, 1 is, by the mutual attractions of almost equal proportions of oppositively-charged centres, to bring the keratin main chains into as folded a state as the co-valent cross-linkages

Mr. Neale (Manchester) said: I wish to express my appreciation of Dr. Jordan Lloyd's treatment of the swelling and hydration of the protein structure. I feel confident that a similar approach to the problem of swelling of cellulose in alkalis would be a most valuable addition to the insight we have already obtained into the mechanism of

this process by the use of the Donnan Equilibrium.

Dr. J. R. Katz (Amsterdam) said: The interesting facts Miss Lloyd has described with regard to the hydration of proteins are important for the theory of swelling. Many of the facts she calls hydration I should call swelling. This word has been introduced into science by famous botanists (1858-1880), by Nägeli, Pfeiffer, Reinke, Hugo de Vries, and I think they have given such a clear definition of swelling that we must go on accepting this name for the phenomenon. Swelling they called the phenomenon that a solid may take up a liquid without losing its apparent homogeneity, while its dimensions become enlarged and while its cohesion becomes lessened.2 I would like to reserve the word hydration for the molecular phenomenon, the combination between the protein molecules and the water molecules.

Besides this, it may be useful to remember the X-ray data about the swelling of collagen and gelatine, as they make it understandable that even in the solid state the molecules of a protein may combine with water molecules. The crystal lattice of these two substances varies with the degree of swelling, and varies as a continuous function of the degree of swelling (the water content) of these substances.3 Therefore, in such substances, swelling is not only an intermicellar phenomenon, but the micellae themselves swell. The water can permeate the solid substance like in a solution; intramicellar swelling is very much the same as solid solution.

In silk, however, the crystalline X-ray pattern is not changed

through swelling in water.

Dr. Jordan Lloyd, in reply, said: The mutual interactions of the side chains of proteins are still a subject for future research rather than present speculation. At the moment, the co-valent cross link through the sulphur atoms of cystine residues appears to be reasonably well established and the main interest is centring on the possible link between

<sup>&</sup>lt;sup>1</sup> See Some Problems in the X-ray Analysis of the Structure of Animal Hairs

and other Protein Fibres, and also my remarks on the paper "The Constitution of the Keratin Molecule," by J. B. Speakman and Mercia C. Hirst.

<sup>2</sup> See my paper on the "Laws of Swelling," under paragraph 1, page 279.

<sup>3</sup> O. Gerngross, K. Hermann and W. Abitz, Z. physik. Chem., 10B, 371, 1930; J. R. Katz and J. C. Derksen, Recueil trav. chim. Pays-Bas, 51, 513, 1932; E. Nähring, Z. mikrosk.-anatom. Forschung, 23, 439, 1930.

carboxyl and amino groups at the ends of the side chains. It is important to notice that this link may be electro-valent or co-ordinated:—4

The sharp difference between the value of the ionisation constant of the tetra-substituted ammonium bases and of the unsubstituted or mono-, di-, or tri-substituted bases suggests that as long as the ammonium ion has a hydrogen available it will readily co-ordinate with an anion. The co-ordinated link shown above may, therefore, be assumed to be present in large amount, even in dilute solutions, and will be the predominant form when the concentration of water is low as in fibres. This link will not be so heavily hydrated as the corresponding electro-valent link and will have definite length and direction. It would possess the characteristics of the link referred to by Dr. Astbury, namely in a fibrous protein it would be occupied in holding together the original structure while in a hydrolysate of the same protein it would appear as charged centres.

<sup>4</sup> P = protein backbone.

# THE CONSTITUTION OF THE KERATIN MOLECULE.

By J. B. Speakman, D.Sc., and Mercia C. Hirst, Ph.D.

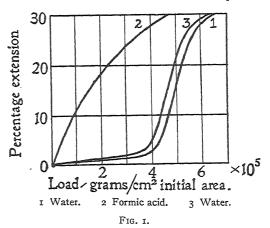
Received 21st July, 1932.

The wool fibre is now known to consist of micelles which are long in comparison with their thickness. They are probably lamellar in shape, their thickness does not exceed 200 Å.U., and they are arranged with their long axes parallel to the length of the fibre. Although the constitution of the micelles is still unknown, X-ray analysis of wool and related animal hairs has led Astbury to suggest a fundamental principle of protein structure, which accounts successfully for the elastic properties of wool and silk and gives a new significance to the preponderance of  $\alpha$ -amino acids among the products of protein hydrolysis. Proteins are assumed to consist essentially of long peptide chains having the general formula:—

The specific properties of any particular protein are determined by the configuration of the peptide chain and the constitution of the side chains ( $R_1$ ,  $R_2$ , etc.), whose nature depends on the  $\alpha$ -amino acids from which they are derived. In the case of the wool fibre, the peptide chains, which are coiled into a series of pseudo hexagons, are arranged parallel to its length, and cohesion within the micelle is determined either by van der Waals forces between the peptide chains and their side chains, or by chemical combination between the side chains of adjacent peptide chains.<sup>3</sup>, <sup>23</sup>

It has recently been shown that acids have a peculiar action on the micelles of the wool fibre.¹ In formic acid, for example, the fibre swells to a striking degree, the Hooke's Law section of the load-extension curve disappears, the fibre acquires a rubber-like elasticity and plasticity is at a minimum. Silk, immersed in formic acid, shows similar properties, but in this case it is also known that the X-ray fibre diagram disappears. By analogy with silk it was argued that the crystal structure of wool must similarly disappear in formic acid and Astbury has since confirmed the deduction. Such observations can be explained

only by assuming that peptide chains within the micelles are separated by the action of acid, i.e. a kind of micelle subdivision takes place. The degree of subdivision is unknown, but since the wool fibre is not dissolved by formic acid in the cold, subdivision to simple peptide chains can scarcely have occurred. great a degree of subdivision is in event improbable be-



cause cystine must form one of the side links between adjacent chains, and subdivision to pairs of chains linked laterally by the cystine molecule is the greatest degree of subdivision to be expected.

The most interesting feature of the action of acids on wool, however, is not that they possess this property of subdividing the micelles, but that their action is almost completely reversed by prolonged washing of the fibre in running water. The phenomenon is illustrated by the three load-extension curves of Fig. 1, representing the properties of the same wool fibre first in distilled water, then in 98-100 per cent. formic acid, and finally again in distilled water after prolonged washing in running water.

It is clear that acids are capable of separating the peptide chains of the micelles of the wool fibre against their cohesive forces; and if the peptide chains are linked together chemically through their side chains, such side linkages as are opened by acid must have the ability to reform spontaneously when the acid is removed. Whatever may be the nature of the cohesive forces between the peptide chains, it is evident that a study of the action of acids on wool is capable of giving information as to their character.

# Experimental.

# (a) Technique.

The above preliminary survey of the action of acids on wool was carried out with purely arbitrary concentrations of different acids selected at In the present endeavour to elucidate the nature of the cohesive forces within the micelle, a study was first made of the extent of micelle subdivision as a function of the  $p_{\rm H}$  of the environment, with acids of various strengths. For this purpose, the technique followed in earlier investigations of the structure of the wool fibre was again adopted.4 Fibres, uniform in diameter along the length, were selected from Cotswold wool which had been purified by successive extraction with alcohol, ether and water. In each case, the cross-sectional area was estimated by making thirty measurements of diameter along the 5-centimetre length used to determine the load-extension curve. Calibration was carried out under desorption conditions in a room maintained at 65 per cent. relative humidity and 22.2° C.

The load-extension curve of each fibre was first determined in distilled water ( $p_{\rm H}$  5.5) at 22.2° C., using a rate of loading of 1  $\times$  10<sup>5</sup> g./cm.<sup>2</sup> per minute, extension being limited to 30 per cent. because it has been shown that wool fibres undergo serious permanent alteration in elastic properties when stretched beyond this point.4 Each fibre was then immersed in a large volume of acid solution of known  $p_{\rm H}$ , the latter being determined potentiometrically by means of the hydrogen electrode, or the quinhydrone electrode, according to the nature of the acid used. After twenty-four hours, during which time the acid solution was renewed at intervals, the load-extension curve of each fibre was redetermined in the solution with which it had come to equilibrium. The two load-extension curves were then used to evaluate the work (W) needed to perform a 30 per cent. extension in water and in acid solution. The difference between the two values of W gives a measure of the extent of reaction with acid, and it is convenient to express this difference as a percentage of the work needed to stretch the fibre in water at the standard  $p_{\rm H}$  (5.5). Such a method of treating the results has the merit of eliminating possible errors in estimating the cross-sectional area of wool fibres from the comparison of various acid solutions in reaction with wool.

# (b) p<sub>H</sub>-Stability Curve.<sup>5</sup>

By means of the ultra-centrifugal method developed in his laboratory, Svedberg 6 has measured the stability of a number of soluble proteins as a function of the  $p_H$  of the environment. Each of the monodisperse proteins was found to be stable over a fairly wide range of  $p_{\rm H}$ , called the  $p_{\rm H}$ -stability region, which includes the isoelectric point. The technique described above affords a means of extending Svedberg's observations to the insoluble proteins, and since his experiments have not been confirmed by any independent method, an additional interest is associated with the properties of wool keratin. For these reasons, the first experiments to be carried out were not limited to the action of acids on wool but covered a wide range of  $p_{\mathbf{H}}$ . The method of experiment was that already described, two determinations of the percentage reduction in the work required to perform a 30 per cent. extension being made at each  $p_{\mathbf{H}}$  with different fibres, and the average taken. A summary of the results is given in Table I.

TABLE I.

Reagen	t.			$p_{ m H}$ .	Work Reduction. Per Cent.
Sulphuric acid			-	7∙96	33.8
,, ,, ,	•	•	.	0.57	33.9
,, ,, .		•	.	1.06	33.2
,, ,, •	•	•	-	1.85	30.2
,, ,, .		•	.	2.09	24.3
,, ,, ,		•	. ]	2.98	9.4
,, ,, ,,			. 1	3.55	2.7
,, ,,			.	4.02	I·4
,, ,,			. 1	4.55	1.5
,, ,,			. 1	5.36	1.1
Distilled water				5.48	1.2
Borax	_			7.40	1.1
	-		.	8.02	2.2
Sodium carbonate			.	8.58	3.0
Borax	•	•		9.19	6.0
odium carbonate	•	•	. 1	10.18	5.8
	•	•	1	10.62	9.8
"	•	•	.	11.07	13.2
`onetic ando	•	•	. [	11.86	16.3
Caustic soda .	•	•	. 1	12.82	•
,, ,, .	•	•	•	12.02	53·1

From the graph, Fig. 2, it is evident that wool is immune to the action of acid and alkali between  $p_{\rm H}$  4 and  $p_{\rm H}$  8 (approx.). The micelles undergo no subdivision within these limits although combination with acid is known to begin at  $p_{\rm H}$  4.8. Detailed discussion of the  $p_{\rm H}$ -stability curve must be deferred until later in the paper, but the preceding experiments served to show that alkali is unsuitable for precise study of the constitution of wool keratin. The load-extension curves of fibres in alkaline solution indicated quite clearly that attack in such cases is not limited to the side linkages between peptide chains, the latter being themselves attacked as would be expected from their constitution.

# (c) The Donnan Equilibrium.

Although sulphuric acid, like formic acid, is capable of facilitating fibre extension by its action in separating the peptide chains of the micelles, the weaker formic acid is twice as effective at  $p_{\rm H}$  0.0. In order to discover the reason for this peculiarity, and to generalise the observations, attention was next directed to the influence of the strength of the acid on its reaction with wool. A number of acids were chosen, ranging in strength from hydrochloric acid ( $K=10^7$ ) to acetic acid ( $K=1.8 \times 10^{-5}$ ), and the elastic properties of the wool fibre studied as before in solutions of known  $p_{\rm H}$ . The results are summarised in Table II.

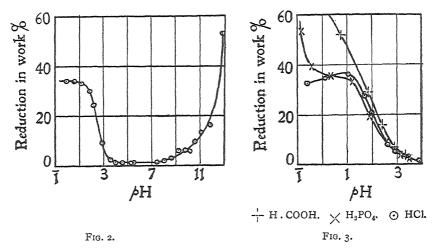
The data for hydrochloric, phosphoric and formic acids are illustrated in Fig. 3, and it is evident that the action of acids in facilitating fibre extension increases smoothly with decreasing ionisation constant. For example, the curve for hydrochloric acid shows a maximum at  $p_{\rm H}$  1.0, that for sulphuric acid (Fig. 2) is flat below  $p_{\rm H}$  1.0, whereas the curve for phosphoric acid first tends to become flat and then shows a rapid rise below  $p_{\rm H}$  0.0. Finally, the curves for chloracetic, formic and acetic acids all show a continuous rise with decreasing  $p_{\rm H}$ , the slope becoming steeper with acids of decreasing ionisation constant. Glycollic acid is exceptional in character, but this may be due to the hydroxyl group, which is known to have a specific action on wool.

TABLE II.

		ADLE II.	
Acid.	₽ <sub>K</sub> .	$p_{ m H}$ .	Work Reduction. Per Cent.
Hydrochloric acid .	(K = 10 <sup>7</sup> )	ī·35 o·08 i·02 i·68 i·98 2·63 2·95 3·90	32·9 34·7 36·1 27·2 20·8 7·7 5·3 1·3
Oxalic acid	1·42	0·62 1·06 1·90 2·56 3·28 3·80	37·0 34·1 24·4 11·0 4·3 2·3
Sulphuric acid	1.77	See Table I.	
Phosphoric acid .	2.0	ī·14 ī·56 o·36 I·20 I·90 2·59 3·12 3·46	53°5 39°5 35°9 33°3 19°7 8°8 3°6 2°2
Mono-chloracetic acid	2.8	T·65 0·98 1·65 2·14 2·55 3·02	53·1 37·3 26·6 16·8 9·3 3·3
Formic acid	3*7	0·76 1·84 2·41 2·90 3·37 4·53	51.7 28.9 15.8 6.6 3.6 2.4
Glycollic acid	3.8	T·56 0·69 1·21 2·03 2·57 3·03	44°0 37°7 34°1 18°6 8°4 3°9
Acetic acid	4.7	1·12 1·96 2·61 3·05 3·69	46·9 25·3 8·5 3·4 1·6

The fact that the reduction in the work required to stretch fibres in hydrochloric acid solution reaches a maximum at  $p_{\rm H}$  I·O and then falls, suggests at once that the degree of swelling of the fibre plays some part in determining its resistance to extension; for according to the Procter-Wilson theory, the swelling of proteins in solutions of strong acids must first increase, reach a maximum, and then diminish as the hy-

drogen-ion concentration is increased. The same theory is capable of explaining the greater effectiveness of weak acids in facilitating fibre extension. Since wool and its ions are non-diffusible, the necessary



conditions for the establishment of a Donnan equilibrium are present, and if the equilibrium concentrations of the several ions are represented by the algebraic symbols in the diagram, then  $x^2 = y(y + z)$ .

$$\begin{array}{c|c} (z) W^{+} \\ (z) Cl^{-} \\ (y) H^{+} \\ (y) Cl^{-} \\ (fibre) \end{array} | \begin{array}{c} H^{+}(x) \\ Cl^{-}(x) \\ (medium) \end{array}$$

The excess concentration of diffusible ions inside the fibre determines the extent of swelling and is given by the expression

$$e = 2y + z - 2x = \frac{(x - y)^2}{y}$$
.

With weak acids, such as acetic acid, the wool forms highly ionisable salts which depress the ionisation of the free acid inside the fibre, so that y is small and (x-y) is large. The quantity  $e=\frac{(x-y)^2}{y}$  is therefore large and swelling is extremely high. It is evident, therefore, that the swelling of wool fibres at the same  $p_{\rm H}$ , but in different acids, will vary inversely as their ionisation constants, and the action of weak acids in reducing the resistance to extension of the wool fibre to a greater degree than strong acids finds a simple explanation on this basis. It need hardly be said that direct observation confirms the preceding deductions—the maximum increase in diameter of wool fibres on transference from water to sulphuric acid is 2 per cent., whereas with formic acid the increase is 50 per cent. or more.

The applicability of the Procter-Wilson theory of swelling to the action of acids on wool does not necessarily imply that strict chemical compounds are formed between wool and acids. Indeed, the evidence so far advanced in this paper has little or nothing to say regarding the mode of combination of acids and wool, and all the preceding phenomena

can be "explained" in terms of swelling without further inquiry. Nevertheless, one striking fact emerges which demands further discussion. Although the swelling of wool fibres in sulphuric acid is so small compared with that in formic acid, the latter is only twice as effective in facilitating fibre extension. This suggests that the first action of all acids on wool is essentially the same and causes a reduction in the resistance to extension. Superimposed on this first effect is that of swelling, which is specific for each acid according to its ionisation constant.

# (d) Depression of Swelling.

I. Neutral salt action.—The validity of the preceding hypothesis can be examined by studying the action of acids on wool in the absence of swelling. A possible method is to use neutral salts in conjunction with acid, the neutral salt having the effect of depressing swelling without necessarily interfering with the action of acid. Accordingly, the elastic properties of wool fibres were studied in N/5 NaCl solutions containing varying amounts of hydrochloric acid. In view of the great interest of the resulting data, the experiment was extended to include alkaline solutions and the complete set of results is summarised in Table III.

TABLE III.

Reagent.					$p_{\mathbf{H}^{\bullet}}$	Work Reduction. Per Cent.
HC1 + N	/5 NaCl		•		0.01	32.6
,,	,,	•		.	1.00	35.3
,,	,,	•			1.71	36.5
,,	,,	•	•	-	1.97	31.2
,,	,,			- 1	2.72	21.1
,,	>7			.	3.02	18.6
,,	,,			.	3.83	9.9
,,	,,	•	•		4.95	2:2
Na <sub>2</sub> CO <sub>3</sub> -	⊢ N/5 N	aCl			7.00	1.5
,,	,	,	•		8.77	3·7 8·8
,,	,	,			9.97	1
,,	,	,		.	10.59	12.2
		,		.	10.97	15.4
NaOH +	N/5 Na	aCI.	•	.	11.59	22.7
,,	,,			.	12.00	25.1

The data are graphed in Fig. 4 along with the corresponding results for hydrochloric acid and alkaline reagents in absence of common salt. An examination of the two curves reveals a number of interesting points. In the first place, it has to be remembered that the  $p_{\rm H}$  within the wool fibre is incapable of direct measurement, and all recorded values are those of the media with which the wool was in equilibrium. But in presence of salt, the  $p_{\rm H}$  inside and outside the fibre approximate to one another, so that the curve relating to salt solutions always lies inside the other. Despite the action of salt in minimising differences of  $p_{\rm H}$  and in reducing swelling, the maximum reduction in the resistance to extension of wool fibres in hydrochloric acid solution is precisely the same in presence and absence of salt. Swelling is not entirely eliminated, however, and below  $p_{\rm H}$  1.6 the curve shows a fall similar to that in absence of salt. Nevertheless the fact that swelling can be reduced without interfering with

the action of acid in facilitating fibre-extension is a confirmation of the view that swelling is not the primary cause of a reduced resistance to extension.

A second important feature of the curve is that the range of the  $p_{\rm H}$ -stability region is reduced in presence of salt and occupies only  $p_{\rm H}$  5 to 7 instead of  $p_{\rm H}$  4 to 8. The action of acid begins at  $p_{\rm H}$  5·0, in good agreement with the value of 4·8 obtained in 1925  $^9$  for the point at which combination with acid commences. Although no data could be obtained for the alkali side, the isoelectric point of wool was provisionally defined as  $p_{\rm H}$  4·8. The isoelectric point was subsequently redetermined by Meunier and Rey,  $^{10}$  who gave the value  $p_{\rm H}$  3·6 to 3·8, afterwards modified to  $p_{\rm H}$  4·0 to 4·5. A more recent determination by Elöd and Silva  $^{11}$ 

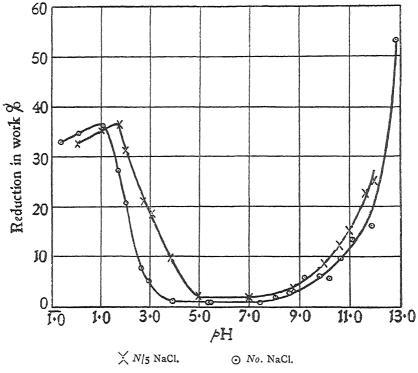


FIG. 4.

agrees precisely with that established in 1925, and it has come to be recognised that the isoelectric point of wool is at  $p_{\rm H}$  4.8. This view now needs modification. From the curve relating the ease of extension of wool fibres to the  $p_{\rm H}$  of N/5 sodium chloride solutions containing varying amounts of hydrochloric acid, it is evident that combination with acid begins at  $p_{\rm H}$  5.0 or thereabouts. Using the same argument with reference to the alkali side of the curve, it seems probable that combination with alkali commences at  $p_{\rm H}$  7.0. In other words, wool does not possess an isoelectric point but an isoelectric region from  $p_{\rm H}$  5 to  $p_{\rm H}$  7. Further evidence in support of this view will be given later in the paper.

The diminution in the range of the  $p_{\rm H}$ -stability region in presence of salt is, in part, due simply to its action in making internal and external

 $p_{\mathbf{H}}$  identical. It is, however, more than doubtful whether this is the whole explanation because, at  $p_{\rm H}$  4.8, internal and external  $p_{\rm H}$  are identical even in absence of salt, and both curves should originate in this point. That this is not so seems to indicate that salt does not function simply in the way specified above. Such a deduction is supported by the work of Csapo, 12 who found that considerably more acid is fixed by gelatin in presence of salt than in its absence. Similarly, Gerngross and Loewe 13 found an increased fixation of alkali by hide powder in presence of neutral salts. The action of neutral salts on wool clearly requires further investigation, and there is some probability that it will serve to explain the origin of  $p_{\rm H}$ -stability regions in general.

2. Diazotised wool.—Attention was next turned to diazotised wool as a possible means of studying the action of acid in the absence of swelling. The load-extension curves of single wool fibres were first determined in water at  $p_{\rm H}$  5.5. After being allowed to return to the original length, each fibre was diazotised separately in a mixture of 50 c.c. I-042 N/I H<sub>2</sub>SO<sub>4</sub> and IO c.c. N/I NaNO<sub>2</sub> for sixteen and a half hours. After being washed in running water for twenty-four hours to remove all traces of acid, the fibres were again stretched in water at the standard  $p_H$ . Although the two load-extension curves were thus determined at the same  $p_{\rm H}$ , the work required to perform a 30 per cent. extension was 17 per cent. less after diazotisation. Hence nitrous acid has precisely the same action as other acids in facilitating fibre extension, except that its effect on the fibre is not reversed by prolonged washing in running water. Lest it should be supposed that the preceding value of 17 per cent. represents the maximum effect of nitrous acid in facilitating fibre extension, it must be emphasised that complete reaction with nitrous acid is not attained except under well-defined con-The concentration of nitrous acid, the  $p_{\rm H}$  of the reaction mixture and the time of reaction all affect the extent of attack. In the preceding experiment, the concentration of nitrous acid is too low to give complete reaction in the time allowed, and the part played by acidity  $(p_{\rm H})$  is well illustrated by the following experiment in which single wool fibres were diazotised in a mixture of 50 c.c. water, 10 c.c. N/INaNO2 and 6 c.c. of 98-100 per cent. formic acid for sixteen and a half hours. Although the concentration of formic acid at the moment of mixing was approximately 2.4 N, yet diazotisation caused only 9.3 per cent. reduction in the work needed to perform a 30 per cent. extension in water. The reason for this is, as already indicated, that the  $p_{\rm H}$  given by the relatively high concentration of formic acid is greater than that of N/I sulphuric acid. Such properties are by no means peculiar to wool: they have already been subjected to detailed study by Plimmer 14 in the case of amides and other amino compounds.

Despite the fact that nitrous acid is able to facilitate fibre extension in much the same way as other acids, the swelling of diazotised wool fibres in water at  $p_{\rm H}$  5.5 is identical with that of untreated fibres, within the limits of microscopic measurement. Actually, the amount of water adsorbed by diazotised wool from atmospheres at different humidities up to saturation is always less than in the case of untreated wool. This would suggest that the swelling of diazotised wool in water is slightly

less than that of untreated wool.

Such experiments as the preceding make it certain that acids do not facilitate fibre extension merely by promoting increased swelling. In other words, swelling is a consequence and not a cause of micelle subdivision by acid.

# (e) The Adsorption of Acid by Wool.

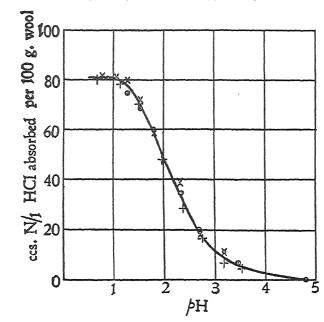
So far, therefore, it has been shown that nitrous acid is similar to other acids in causing a reduction in the resistance to extension, but its effect on the fibre is incapable of being reversed by prolonged washing in running water. This peculiarity is clearly due to the irreversible conversion of amino groups into hydroxyl groups, and the otherwise similar action of nitrous and other acids on wool suggests that all acids react primarily with the free amino groups present. In the case of strong acids like HCl and  $\rm H_2SO_4$ , reference to Figs. 2 and 3 shows that reaction with wool is complete at  $p_{\rm H}$  I·O (external) and if such acids react primarily with the free amino groups present, the amount of acid adsorbed at  $p_{\rm H}$  I·O should be closely related to the free amino nitrogen content of wool as directly determined. Both sets of determinations were therefore carried out as follows.

I. The amount of acid adsorbed.—The wool chosen for experiment was in the form of top and was first freed from adsorbed soap and residual oil by extraction with alcohol and ether in a Soxhlet apparatus. It was then brought to  $p_{\rm H}$  4.8 by means of a dilute solution of hydrochloric acid. Excess liquid was removed by centrifuging the wool, which was then allowed to dry by exposure to the air. Approximate 2-gram samples of wool were transferred to weighing bottles and their dry weights determined by exposure to phosphorus pentoxide for fourteen days in vacuo. Each 2-gram sample was then immersed in 200 c.c. of hydrochloric acid solution of known  $p_{\mathbf{H}}$  and allowed at least two days in which to reach equilibrium, the temperature being 22.2° C. At the end of this time, the wool was removed and the  $p_{\rm H}$  of the solution determined electrometrically. With high concentrations of acid, the change in  $p_{\rm H}$  due to adsorption of acid by wool was too small to allow the amount of acid adsorbed to be calculated with any degree of precision. In such cases, direct titration with alkali was used. The results for Cotswold and Leicester wools were obtained in this way and are given in Table IV. The latter also includes data for South Devon wool, obtained in conjunction with Mr. A. E. Battye, using slightly different experimental conditions. The volume of solution used with each 2-gram sample of wool was only 100 c.c. and the temperature 25° C., but since the only significant difference is that of temperature, and as this is small, the results are included for comparison.

TABLE IV.

Cots	Cotswold.		icester.	South Devon.		
<i>₽</i> <sub>Ħ</sub> .	C.c. N/1 Acid Adsorbed per 100 g. Wool.	₽ <sub>H</sub> .	C.c. N/ r Acid Adsorbed per roo g. Wool.	<i>p</i> <sub>H</sub> .	C.c. N/I Acid Adsorbed per 100 g. Wool.	
0.75 0.89 1.28 1.54 1.80 2.33 2.70 3.18	80·7 80·8 74·7 68·5 60·1 34·9 20·2	0·78 1·08 1·28 1·54 1·81 2·32 2·71 3·17	81·9 81·8 80·0 72·1 59·0 38·8 18·5	0.66 1.15 1.52 1.99 2.38 2.75 3.17 3.55	80·5 78·6 70·5 47·8 28·6 16·4 6·7 4·7	

In Fig. 5, the amount of acid adsorbed is shown as a function of the  $p_{\rm R}$  of the equilibrium solution, a mean curve being drawn through the data for the several wools. Much work has been done on the subject of acid adsorption by wool, but this is apparently the first complete titration



∠ Leicester wool. 

- South Devon wool. 

○ Cotswold wool

Fig. 5.

curve be obtained. form shows quite clearly that combination of wool with acid complete at  $p_{\rm H}$ I.O when 80 c.c. of N/I acid are adsorbed bv 100 wool. g. This result is in good agreement with that Meyer,15 based work which no tempt was made study adsorption as function of  $p_H$ .

If the amount of hydrochloric acid adsorbed by wool from solutions of varying p<sub>H</sub> is

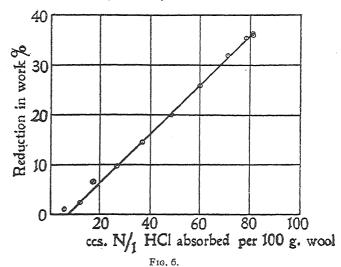
plotted against the corresponding values for the reduction in the work required to perform a 30 per cent. extension (Table II.), a linear relationship is found to hold between the two, as shown in Fig. 6. Each molecule of hydrochloric acid combined with wool therefore contributes a definite quantum to the total reduction in the resistance to extension observed in strongly acid solutions. A stoichiometric relationship of this kind affords strong evidence in favour of the view that the process of acid adsorption by wool is one of strict chemical combination.

2. The free amino nitrogen content of wool.—Van Slyke and Birchard <sup>16</sup> have shown that the free amino nitrogen content of a number of proteins corresponds very closely with half the lysine nitrogen. The conditions of experiment—particularly as regards the time of reaction—were, however, such as to preclude the evolution of nitrogen from arginine. If the time of reaction is increased, arginine gives off increasing quantities of nitrogen and, according to Plimmer, <sup>17</sup> the amount evolved in twenty-four hours corresponds approximately with two reacting nitrogen atoms. In the case of wool, which contains arginine and lysine, the free amino groups from both sources must take part in acid adsorption. For purposes of correlation with the amount of acid adsorbed, estimation of the free amino nitrogen in wool must therefore be carried out under conditions such that arginine, as well as lysine, will react with nitrous acid. In the light of Plimmer's observations, it was decided to estimate free amino

nitrogen in wool by means of the usual van Slyke reagent, allowing the reaction to proceed for twenty-four hours. Using the technique due to Meunier and Rey, <sup>10</sup> the value found for untreated Cotswold wool was 0.94 per cent. Plimmer <sup>14</sup> has also shown that the rate of evolution of nitrogen from compounds such as arginine increases with the acidity of the reaction mixture. Similar experiments have recently been carried out with wool, <sup>18</sup> with similar results, but all the curves showing the amount of nitrogen evolved as a function of the time of reaction, converged to give a limiting amount of free amino nitrogen of 0.92 per cent. The concentration of sodium nitrite was, however, only half that employed by van Slyke, and when the full concentration was used, a limiting amino nitrogen content of 1.19 per cent. was found. In all probability, this value is too high because the form of the curves, showing the rate of evolution of nitrogen, suggested that actual decomposition of the wool had taken place to a small extent. There can, however, be no doubt that the free

amino nitrogen content of wool lies between 0.92 per cent. and 1.19 per cent., the lower value being more nearly correct.

If wool contains 0.92 per cent. of free amino nitrogen, the amount of hydrochloric acid adsorbed by wool on this account should be 65.7 c.c. of N/I acid per IOO grams.



Adsorption of acid is, however, not limited to combination with free amino groups: according to Vickery and Block,  $^{19}$  wool contains 0.66 per cent. of histidine, and an additional 4.3 c.c. of N/I acid per 100 grams of wool would be adsorbed on this account. Thus, using the minimum value for the free amino nitrogen content of wool, the calculated amount of hydrochloric acid adsorbed when combination is complete is 70 c.c. of N/I acid per 100 grams. In order to give complete agreement with the experimental value of 80 c.c., the amino nitrogen content of wool would have to be I.06 per cent., a value lying midway between the two values given above. It is thus possible to account somewhat precisely for the amount of acid adsorbed by wool in terms of its content of histidine and free amino nitrogen.

If Astbury's hypothesis  $^2$  of long-chain protein molecules is correct, the  $\alpha$ -amino groups of arginine and lysine must be bound into these molecules, leaving the terminal amino groups free for combination with acid. Hence the amino nitrogen of wool is derived from the guanidine group of arginine and the  $\epsilon$ -amino group of lysine. The arginine and lysine content of wool have been determined by various workers, and

there should be close agreement between the amount of free amino nitrogen in wool, calculated from its arginine and lysine content, and the direct determination. The appropriate data are summarised in Table V.

Observer.	Percentage b	Calculated Free Amino Nitrogen.	
	Arginine.	Lysine.	Per Cent.
Vickery and Block <sup>19</sup> (wool) Marston <sup>20</sup> (wool)	7·8 10·2 6·0	2·3 2·8 2·2	0·85 1·09 0·70
Vickery and Leavenworth <sup>22</sup> (human hair)	8∙o	2.5	0.88

TABLE V.

Such results suggest that the arginine and lysine content of different wools may be variable, but it is apparent that the free amino nitrogen of wool can be accounted for more or less precisely in terms of its arginine and lysine content. This is especially true since Vickery suspects his determinations to be low, at least in the case of human hair.

There is thus a close relationship between the amount of free amino nitrogen in wool, its arginine and lysine content, and the amount of acid adsorbed when combination is complete.

# (f) The Constitution of the Keratin Molecule.<sup>23</sup>

Knowing that the hydrochloric acid adsorbed by wool combines mainly with the terminal amino groups of arginine and lysine, it is neces. sary to inquire how this reaction is able to facilitate fibre-extension. Since the  $\alpha$ -amino and carboxyl groups of both these acids (and histidine) are assumed to be embodied in the long peptide chains (vide supra), the terminal amino groups are in each case part of a side chain and they may, or may not, be combined with the side chains of adjacent peptide chains. If the amino groups remain uncombined, their dissociation constants will be those of the free amino acids:

arginine . . . 
$$k_b = 1 \times 10^{-5}$$
  
lysine . . .  $k_b = 3.2 \times 10^{-5}$ 

and combination of wool with acid should be complete at  $p_{\rm H}$  7. Actually, combination with acid does not begin above  $p_{\rm H}$  5.0.

Conversely, if the terminal amino groups of the side chains are free, the basic dissociation constant of wool should be approximately  $I \times I0^{-5}$ . The true value can be deduced as follows. It has already been shown that the reduction in the resistance to extension of fibres is strictly proportional to the amount of acid adsorbed at the same  $p_{\rm H}$  (Fig. 6). Hence although the dissociation constant of wool cannot be deduced directly from the acid adsorption curve of Fig. 5, because of the difference between internal and external  $p_{\rm H}$ , it can be deduced from the elastic properties of wool in salt solutions where internal and external  $p_{\rm H}$  are identical. Referring to Fig. 4, it is evident that combination of wool with hydrochloric acid is complete at  $p_{\rm H}$  1.70, where the reduction in the resistance to extension is 37.0 per cent. When due allowance is made for the action of salt in facilitating extension at  $p_{\rm H}$  5, it is clear that the wool is half-combined with acid when the reduction in the resistance to extension is 19.25 per cent., i.e. at  $p_{\rm H}$  2.85. The basic dis-

sociation constant of wool is therefore  $7 \cdot I \times 10^{-12}$ , far removed from the values for free amino groups in the side chains. On the other hand, the dissociation constants of the  $\alpha$ -amino groups of arginine and lysine are  $2 \cdot 2 \times 10^{-12}$  and  $1 \cdot 0 \times 10^{-12}$  respectively. Their behaviour as

weak bases is due to the zwitterion constitution NH3-R-COO, the amino group being already combined, in effect, with the carboxyl group. It thus becomes certain that the terminal amino groups of arginine and lysine are not uncombined in the wool fibre, and since the basic dissociation constant of wool is similar in magnitude to that of the α-amino group of arginine and lysine, it seems probable that they are combined with carboxyl groups. The latter are derived from the side chains of adjacent peptide chains, which are thus linked together by salt linkages of the type: R<sub>1</sub>-NH<sub>3</sub>-COO-R<sub>2</sub>. Such carboxyl groups as are needed to combine with the free amino groups of arginine and lysine, as well as with histidine, must be derived from dicarboxylic acids. According to Abderhalden, wool contains 12.9 per cent. of glutamic acid and 2.3 per cent. of aspartic acid, but these values are known to be low. If wool contains 1.06 per cent. of free amino nitrogen, the amount needed to account completely for the acid adsorbed at  $p_H$ I.O. the quantity of glutamic acid required to form salt linkages is II-I per cent. To this must be added 0.6 per cent. for combination with histidine, giving a total of 11.7 per cent. There is thus more than enough glutamic acid in wool to form side linkages of the type described above, but it has to be remembered that wool contains 1.2 per cent. of amide nitrogen which is usually assumed to be combined with dicarboxylic acids in the form of an acid amide. The excess of 1.2 per cent. of glutamic acid and 2.3 per cent. of aspartic acid would together combine with 0.35 per cent. of amide nitrogen. Since Abderhalden's determinations of aspartic and glutamic acid in wool are known to be low, it can safely be assumed that enough of these acids will be found present in wool to account quantitatively for the amide nitrogen as well as for what is needed to combine with arginine, lysine and histidine.

It now seems certain that one of the side linkages between the long peptide chains of the wool molecule is a salt of arginine and glutamic acid, qualified by the fact that arginine may be replaced by lysine or histidine and glutamic acid by aspartic acid. The formula of the linkage is given below, using arginine and glutamic acid as typical units:

At the time when a linkage of this type was first suggested, 23 evidence of a striking confirmatory character appeared in the literature. Frankel 24 has been able to prepare salts of arginine with glutamic acid and aspartic

acid of the type described above and they retain their existence in aqueous solution. He goes so far as to suggest that "the discovery of solid molecular compounds between amino acids, and their existence in solution also, compels the fact of intermolecular salt formation to be taken into account in any consideration of the molecular cohesion of solid proteins." In addition, he suggests that salt formation of this type is concerned in the formation of protein micelles, and there can be no doubt that the micelle of the wool fibre affords a striking confirmation of his deductions.

# (g) The Properties of the Linkage.

I. Hydrolysis.—It is important to note that until recently the possibility of salt linkages playing any significant part in protein structure was rejected because the acid and basic dissociation constants of proteins in general are extremely small, and such linkages would be hydrolysed in water. The misconception has arisen because of the peculiar properties of the zwitterion, and it is now recognised that proteins possess fairly strong acid and basic properties. For example, when acid is added to a protein, the ionisation of the acid group of the zwitterion is depressed, and what has been regarded as the titration curve of a weak base is, in reality, the back titration curve of a fairly strong acid. In the case of wool, the zwitterions are derived from the salt linkage of arginine (lysine or histidine) and glutamic acid (aspartic acid). Taking the case of arginine and glutamic acid, the dissociation constants of the acid and base involved in salt formation are  $6.3 \times 10^{-5}$  and  $1 \times 10^{-5}$ . The degree of hydrolysis of the resulting salt in water will therefore be

$$y = \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{10^{-14}}{6 \cdot 3 \times 10^{-10}}} = 0.004 \text{ or 0.4 per cent.}$$

Even in the extreme case of histidine and glutamic acid, the degree of hydrolysis is only 16.7 per cent. The argument that salt formation between amino acids can play no significant part in protein structure because of the hydrolysis which must occur in water, thus loses the whole of its significance.

2. The  $p_{\rm H}$  stability region.—Reference to Fig. 4 shows that the slope of the acid side of the  $p_{\rm H}$ -stability curve is much steeper than the alkali side. The reason for this is now evident, for when alkali is added to wool the basic groups of histidine, arginine and lysine are back-titrated. These compounds differ greatly in basicity, histidine being weak and lysine strong. Hence the first effect of alkali is to depress the ionisation of histidine as a base, followed by arginine and lysine. The titration curve, and therefore the  $p_{\rm H}$ -stability curve, is extended over a wide range of  $p_{\rm H}$ in consequence, and remains fairly flat until arginine and lysine begin to enter into the reaction. The latter are such strong bases that complete repression of ionisation is not attained before the peptide linkages begin to be attacked. On the acid side, however, only two acids are concerned, aspartic and glutamic, and their dissociation constants are not widely separated, the values being  $1.5 \times 10^{-4}$  and  $6.3 \times 10^{-5}$  respectively. The acid titration curve is therefore more sharply defined, especially as glutamic acid is present in large excess.

The existence of an isoelectric range between  $p_{\rm H}$  5 and 7 in the case of wool is readily explained on the assumption that the peptide chains are linked across by salts of histidine, arginine and lysine on the one hand, with aspartic and glutamic acids on the other hand. Six types of

salt linkage are possible and each has its isoelectric point. Using the following values for the dissociation constants, the various isoelectric points can be calculated from the formula

$$[\mathrm{H}]_{\mathrm{I.Pt.}} = \sqrt{\frac{K_a}{K_b} \cdot K_w}.$$

Compound.	K <sub>a</sub> .	Compound.	К <sub>b</sub> .	
Glutamic acid . Aspartic acid .	6·3 × 10 <sup>-5</sup> 1·5 × 10 <sup>-4</sup>	Lysine Arginine Histidine	3.2 × 10-5 1.0 × 10-5 5.7 × 10-9	

The results are summarised in Table VI.

TABLE VI.

Salt.	$p_{\rm H}$ of Isoelectric Point.
Histidine—Aspartic acid Histidine—Glutamic acid Arginine—Aspartic acid Arginine—Glutamic acid Lysine—Aspartic acid Lysine—Glutamic acid	4·79 4·98 6·41 6·60 6·66 6·85

It is significant that these values define with some degree of precision the range of the  $p_{\rm H}$ -stability region which, in presence of salt, has been shown to extend from  $p_{\rm H}$  5 to  $p_{\rm H}$  7.

3. Elasticity.—Extension of the wool fibre is accomplished by the uncoiling of the long peptide chains, which are normally folded into a series of pseudo hexagons. Molecular rearrangement of this type is impossible unless the side linkages are capable of free rotation about the long peptide chain, i.e. unless the side linkages are opened at the —COO—NH<sub>3</sub>—group. The fact that a perfectly dry fibre may be extended as much as 30 per cent. of its length without breaking, seems at first sight to present a difficulty on the present hypothesis. It has, however, to be remembered

 $R_2$ —COO ions. During extension, rotation of each half of the side link is possible, but extension is difficult because it has to be accomplished against the full attraction of the ions. When the wool fibre <sup>1</sup> is immersed in water, however, some water enters the micelles and reduces the attrac-

that the salt linkage is ionised in the dry fibre, giving R1-NH3 and

tive force between the oppositely charged —NH<sub>3</sub> and —COO ions by virtue of its high dielectric constant. For this reason alone, the wool fibre is much more easily stretched in water than in dry air, but it must not be assumed that this represents the entire action of water on wool. There can, however, be no doubt that the ions derived from the salt linkages play a large part in determining the electrical conductivity of wool. Finally, in acid solution, the ionisation of the glutamic and aspartic acids in the side link is depressed, and the attraction between the peptide chains diminished in proportion to the number of acid groups displaced

from combination. Alkali functions in a similar manner and both reagents facilitate fibre extension on this account.

4. Technology.—The side linkages identified in this paper have an important part to play in most trade processes. They are clearly of major importance in acid dyeing, not merely because the whole action of acid centres on the linkage, but because the colour acid dyes the fibre by displacing glutamic and aspartic acids from the side link. Indeed, the curve relating the amount of dye adsorbed to the  $p_{\rm H}$  of the dyebath is precisely similar to the acid titration curve (Fig. 5) and the  $p_{\rm H}$ -stability curve (Fig. 4). Where the dyestuff is colloidal, the problem is a little more complicated although fundamentally no different from the simple case of inorganic acids. Similarly, the rupture of the side linkage in acid and alkaline solutions gives a clear and precise interpretation of the action of these reagents in milling. Finally, the ionisation of the link is intimately concerned with the electrical properties of wool, plays a large part in swelling phenomena, and gives a clear interpretation of the action of water in modifying the elastic properties of the fibre.

#### Conclusion.

Much work remains to be done to perfect knowledge of the micelle structure of the wool fibre. The most urgent need is a complete analysis of wool into its constituent amino acids, and work on these lines has been undertaken in this laboratory. Despite the limitations of our present knowledge, it can be stated with some degree of certainty that the micelles of the wool fibre consist of long peptide chains bridged across by salt linkages on the one hand and cystine on the other, the salt linkages being formed from glutamic or aspartic acid and arginine, lysine or histidine. Other types of linkage must exist, and their discovery will go far to perfect knowledge of the constitution of the keratin molecule.

In conclusion, we wish to express our indebtedness to the Government Grant Committee of the Royal Society and to the Clothworkers' Company of London, for grants in aid of the present investigation.

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#### GENERAL DISCUSSION.

Dr. J. B. Speakman (Leeds), in presenting his paper for discussion, said: In calculating the properties of the salt linkages of the keratin molecule, the appropriate dissociation constants of the acids and bases concerned have in each case been derived on the assumption that the zwitterions of all free amino acids are formed from the a-amino group and the nearer carboxyl group. In most cases, there is no reason to doubt the truth of the assumption, especially in view of the inherent stability of a 5-membered ring, but the behaviour of arginine may be peculiar. If the guanidine group is sufficiently strongly basic, there is a possibility of it taking part in zwitterion formation in preference to the α-amino group, and the dissociation constant of the free guanidine group would then be I × 10-1, in agreement with Harris' allocation. Using this value, the iso-electric points of the arginine salts of aspartic and glutamic acids would be at  $p_{\rm H}$  8.35 and 8.61 respectively, outside the stability region. So far as this is concerned, therefore, the value for the dissociation constant of arginine used in the paper is the more satisfactory, but it has to be admitted that the preceding high values for the isoelectric points of the arginine salts have the merit of explaining the gradual rise of the  $p_{\rm H}$  stability curve on the alkali side of the iso-electric region. Clearly no final decision between the two possible dissociation constants can be made without further experiment.

Some justification must also be given for the decision given in the paper that the salt linkages, typified by arginine and glutamic acid, are in the nature of bridges between adjacent long peptide chains. The equivalent weight of wool, as deduced from the amount of hydrochloric acid adsorbed at  $p_{\rm H}$  I·O, is at least 1250. This weight must include approximately ten amino acids, of which one will be basic (arginine) and another, acid (glutamic acid). The distance between the two is sufficiently great for it to be more probable that salt formation will occur between acid and basic groups of adjacent chains, rather than between acid and basic groups in the same chain, although the latter possibility should not be entirely excluded.

**Professor E. Elöd** (Karlsruhe i. B.) said: The isoelectric point of wool investigated by Silva and myself stands at  $p_{\rm H}=4.9$  (not 4.8); it was discovered out of the reaction capacity with the action of watery solutions of increasing  $p_{\rm H}$  values from 0.8 to 8.0. In order to obtain clear effects designedly unbuffered pure acid or alkaline solutions were employed. The swelling minimum of the wool, too, confirms this value, provided the duration of the experiment is sufficiently long for it to attain the equilibrium of the swelling. To obtain the equilibrium in these measurements we had to work 6 days at 20° C. As we have already stated a few years ago, the contrary results (e.g., by Meunier

and Rey) can be explained by the fact that the swelling equilibrium had not yet been reached. It is true that we found (in common with W. König, Diplomarbeit Karlsruhe, 1926) that the part of destroyed protein substance proved to be contained in the solution between the  $p_{\rm H}$  values from about 4.5 to about 8.0 are practically constant and only very small, but that the *final*  $p_{\rm H}$  value of the solutions has always been at about 4.83 to 4.90. From this minimum of the reaction capacity at a constant final  $p_{\rm H}$  value, as well as from the swelling minimum, and from the action of unbuffered solutions on wool, we conclude that the iso-electric point is at  $p_{\rm H}$  4.9. It is, moreover, not very probable that the relatively small amounts of the more strongly basic parts of wool proteins, such as arginine and lysine, which together represent only about 10 per cent. of the wool substance, could provide an explanation for an "isoelectric region" from  $p_{\rm H}$  5 to  $p_{\rm H}$  7.

With diazotised wool the isoelectric point changes as could be expected to more acid values.<sup>1</sup> I may add that the maximum of the acid combination capacity of wool after reaching a *real* state of equilibrium at room temperature has always been found to be at  $p_{\rm H}$  1·3.

Mr. W. T. Astbury (Leeds) said: I should like to congratulate the authors on this valuable paper. It is of particular value to the X-ray study of the structure of wool, because it brings forward just that additional physico-chemical evidence that was needed to complete the picture of keratin which such a study suggests. I have pointed out in my paper "Some Problems in the X-ray Analysis of the Structure of Animal Hairs and other Protein Fibres," contributed to this meeting, that X-ray analysis shows that the keratin of animal hairs exists in two forms, the unextended or α-keratin, in which the polypeptide chains are folded, and the extended or  $\beta$ -keratin, in which they are pulled out into a straight configuration analogous to that found normally in natural silk. These two forms have a common feature, that the larger side-spacing (9.8 Å.), that associated with the lateral extension of the side-chains, is the same for both, from which we may infer that the cross-linkages between the main chains are sufficiently firm to permit folding only in a plane transverse to the directions of the side-chains. The authors argue that the electro-positive centres of the basic sidechains are linked across in salt-linkage with the electro-negative centres of the acidic side-chains, but since the relative proportions of these two types of side-chain are so nearly equal, we are justified in view of the X-ray evidence just mentioned in drawing a still further conclusion, that not only do the charged centres approach as closely as possible laterally, but also longitudinally. We thus arrive at the molecular basis of the long-range elasticity of the wool fibre. The two common forms of keratin can be most briefly expressed by the scheme:-

We can see, too, why wool can be made to contract below its normal unstretched length. Speakman has shown that the equivalent weight

<sup>&</sup>lt;sup>1</sup> See Elöd and Stoll, Z. angew. Chem., 41, 19, 1928.

of wool for HCl is 1250, and since the average weight of the amino-acid residues is about 120,² this means that one basic side-chain occurs on the average about every ten residues. Furthermore, since the basic side-chains and acidic side-chains are roughly equivalent, it means also that the electro-positive and the electro-negative centres are on the average separated by the length of five residues. This length, from the results of X-ray analysis, is about  $\frac{5\times5^{\circ}I}{3}$  Å. in normal wool, that is, about  $8\frac{1}{2}$  Å., a distance well over the closest possible distance of approach of the side-chains. The complete scheme is thus:—

Contracted Wool. Normal Wool. Stretched Wool.

Dr. D. Jordan Lloyd (London) said: Dr. Speakman's demonstration of a p<sub>H</sub> stability range in wool keratin finds a parallel in the stability range of swelling shown by muscle fibres and by collagen. With both these proteins the  $p_{\rm H}$  value of the stability range corresponds closely to that for wool keratin. A certain amount of confusion of thought has arisen through a tendency developed among some workers of identifying the  $p_{\rm H}$  value of external solutions at physico-chemical minima of proteins with the iso-electric point and of extending their conception of iso-electric points to cover long ranges extending over two or three units of  $p_H$ . It should always be remembered that, although the  $p_H$ value of the external solution corresponds with the  $p_{\rm H}$  value of the internal solution of hydrated protein at the iso-electric point in the case of soluble proteins, yet the converse does not necessarily follow in the case of insoluble proteins, when these have a closely packed internal structure. There is no doubt that, at the time it was made, Loeb's generalisation that minima of viscosity, swelling, etc., coincide with the iso-electric point of the protein concerned, was of the greatest value, but it needs modifying in the light of later work, especially modern work on the structure of the protein molecule. The writer has recently been examining the properties of two forms of protein fibre (namely horse hair and silk gut) prepared for surgical sutures. Both these fibres show an extreme resistance to acid and alkalies and maintain a "minimum" swelling over an external  $p_H$  range from I to about II. No one, however, would suggest that either has an iso-electric "point" coinciding with this range! There is no doubt that the swelling

<sup>&</sup>lt;sup>2</sup> See Some Problems in the X-ray Analysis of the Structure of Animal Hairs, etc.

of a protein in acid and alkali depends on the accessibility of its polar groups. This need not be the same for the same protein under all conditions. The theory of the existence of cross linkages is a great help in understanding protein behaviour and the variation in the strength of possible cross linkages will probably, in the future, throw much light on the subject. It is an interesting fact that such a simple process as drying appears to influence the properties of the cross linkages. Both with gelatin gels and collagen fibres, drying diminishes the capacity for swelling and it is an interesting speculation that electrovalent linkages, which theoretically are extensible, may be converted by this means into co-valent linkages which are not. It would be interesting to know if Dr. Speakman considers, for instance, that an arginineglutamic acid salt link might even by way of the co-ordinated form be converted into a peptide link in this way.

Dr. T. R. Bolam (Edinburgh) (communicated): Dr. Speakman and Dr. Hirst apply the Procter-Wilson theory to the swelling of wool fibres and deduce that the great difference between the maximum effect of sulphuric acid and that of formic acid is due simply to the former being a strong and the latter a weak acid. This conclusion appears inadequate

on the following grounds.

In the first place no account is taken of the influence of basicity. A strong dibasic acid such as sulphuric acid may be expected to produce less swelling than a strong monobasic acid, for at the same internal  $p_{\rm H}$  the excess of diffusible ions within the fibre is given by

$$e' = \frac{3}{2}y + \frac{z}{2} - \frac{3}{2}x'$$

in the one case and by e = 2y + z - 2x in the other, and since, according to the Donnan theory,

$$x' = y\sqrt[3]{1 + \frac{z}{y}}$$
 and  $x = y\sqrt{1 + \frac{z}{y}}$ 

it can be shown that e must be greater than e'. In accordance with this result the work of Loeb, Loeb and Kunitz, C. R. Smith, and others, has quite definitely established that under comparable conditions a strong monobasic acid, e.g., hydrochloric acid, gives rise to markedly greater osmotic pressure and swelling in gelatin systems than does sulphuric acid.

The question as to whether the strength of the acid is a controlling factor is therefore best approached by comparison between acids with the same effective basicity, for example formic acid and hydrochloric acid. Actually there is a considerable body of evidence which shows that the maximum osmotic pressure developed by a protein solution containing a monobasic acid is, under comparable conditions, independent of the strength of the acid. Apart from the data of Loeb 6 there is, for example, the careful study by C. R. Smith,<sup>5</sup> in which the same maximum pressure was found for hydrochloric, nitric, salicylic, lactic, formic, and other monobasic acids. It may be pointed out that this somewhat ignored work of Smith was carried out irrespective of its significance for the Donnan theory. Since according to the Procter-Wilson theory the osmotic pressure is the force producing swelling, it

J. Gen. Physiol., 3, 691, 1920-21.
 J.A.C.S., 43, 1350, 1921.
 See Bolam, The Donnan Equilibria, Bell, 1932. 4 Ibid., 5, 655, 1922-23.

follows that, other things being equal, the maximum amount of swelling in wool fibre should be identical for all monobasic acids, and any exceptional behaviour must be due to some factor other than variation in the excess of diffusible ions within the fibre. It would thus appear that the suggestion of Dr. Speakman and Dr. Hirst that swelling in formic acid is extremely high because "The quantity  $e = \frac{(x-y)^2}{v}$ 

. . . is large," is open to objection..

Professor R. A. Peters (Oxford) said: I do not know why Drs. Speakman and Hirst say that "until recently the possibility of salt linkages playing a significant part in protein structure was rejected." Authorities such as Sörensen 7 and Cohn,8 would seem always to have relied upon it. The view that salt linkages between groups other than the α-amino and associated carboxyl exist in wool is very interesting, but does not seem to follow necessarily from the data. The  $p_{\rm H}$  for half-combination of the wool with acid is given here as  $p_{\rm H}$  2.85. This is often called  $p_{\mathbf{K}}'$ . If we accept the "Zwitterion" view of amino-acid constitution, of all possible weakly dissociated basic and acidic groups present only two varieties have a  $p_{K}'$  in solution even approximating to this, namely the -COOH associated with the aNH2 groupings of all amino-acids  $p_{\rm H}$  1.8-2.2, and the second -COOH of aspartic and glutamic acids,  $p_{\rm H}$  4.0 approximately. The latter has too alkaline a dissociation curve therefore to be concerned. The former seems too acid by about  $p_{\rm H}$  I.O. It seems to me that there is no evidence from the titration curve that the second carboxyl groups of aspartic and glutamic acid are concerned. Rather the data point to the action of acid and alkali respectively as titrating the -COOH and aNH, groups of the "Zwitterion." The iso-electric region is then equally well explained as due to chemical combination —CONH— linkage of the terminal -COOH and NH<sub>2</sub> groups.

In any case, I think that it is unwise to assume that the apparent dissociation constant of any group in bulk solution is identical with that at the interface between two phases. In recent attempts to measure such differences  $^9$  I have presented evidence for the belief that such groups behave as weaker bases and acids approximately, a displacement of some  $p_{\rm H}$  3.0 was indicated. It is unlikely that displacement will not be present here; in this case it might amount to  $p_{\rm H}$  1.0, and make the —COOH of the R—CHNH<sub>2</sub>. COOH groups titrate exactly as in the wool

Mr. S. M. Neale (Manchester) said: The fact that an iso-electric "region" of little or no swelling was observed with certain protein bodies finds a parallel in the swelling of cellulose in caustic alkalis. Although theoretical considerations, substantiated by measurements of the absorption of alkali, indicated that swelling should begin in dilute solutions of alkali, the natural cotton fibres showed little or no swelling below 2N concentration. An obvious, though perhaps only partial, explanation of the discrepancy is that the theory deals with the osmotic or swelling pressure, whilst appreciable swelling may depend on a certain pressure being exceeded. The magnitude of such a limiting pressure would of course depend on the internal cohesion of the solid.

<sup>9</sup> Proc. Roy. Soc., 133A, 140, 1931.

 <sup>&</sup>lt;sup>7</sup> C. Rend. Lab. Carlsberg, No. 5, 1930.
 <sup>8</sup> Physiol Reviews, 5, 354, 1925.

Dr. Speakman, in reply, said: By his emphasis on the number of days required by the wool to reach equilibrium with acid in his experiments, Professor Elöd seems to imply that the one day allowed in our experiments with single fibres would be insufficient. This is far from being the case because each fibre was separately immersed in a large volume of solution. Not only was the fibre freely accessible to acid, but the concentration of the solution did not change with time, so that equilibrium was attained very rapidly. Actually, the twenty-four hours allowed for the purpose is far in excess of the necessary time. Where large quantities of wool are immersed in a relatively small volume of solution, equilibrium is attained much more slowly, as we ourselves found in experiments similar to Professor Elöd's. Whether, under such conditions, so long a period as six days is necessary for equilibrium is an altogether different matter. Much depends on the form of the wool and its accessibility to acid, and the fact that wool is slowly attacked by acid in the cold should not be overlooked.

Professor Elöd and I agree in defining the point at which wool begins to combine with acid as  $p_H 4.8$ —his value of 4.9 is sufficiently close to the earlier determination of 4.8 to be regarded as identical. Similarly, in the paper under discussion, we have been successful in recognising the combination of wool with acid below  $p_{\rm H}$  5.0 by its effect on the elastic properties of the fibre. On the other hand, the same study of elastic properties failed to reveal any combination with alkali below  $p_{\rm H}$  7.0. For this reason, we have suggested that wool possesses an iso-electric region from  $p_{\rm H}$  5 to 7, whereas Professor Elöd believes wool to have a true iso-electric point at  $p_{\rm H}$  4.9. Recognising that the titration of wool with acid and alkali represents the back titration of the acid and basic groups, respectively, of the salt linkages, it seems probable that the difference of opinion turns simply on the small percentage (0.66) of histidine present in wool. Between  $p_{\rm H}$  5 and 7, the histidine would be largely displaced from combination with aspartic and glutamic acids, so that between these limits of  $p_{\rm H}$ , combination with alkali might be recognised to the extent of 0.4 c.c. of N/10 alkali per gram of wool. But since the histidine is present in such small quantity, and as its salts are partially hydrolysed in water, displacement of histidine from combination would produce little or no effect on elastic properties. Essentially, therefore, wool may be regarded as having an isoelectric region between  $p_{\rm H}$  5 and 7. For some time we have been attempting to determine the true titration curve of wool with acid and alkali in presence of salt, and the data should provide a complete answer to the point under discussion. The results at present available seem to indicate that the titration curve above  $p_{\rm H}$  7 is precisely similar to the  $p_{\rm H}$ -stability curve given in the paper.

Finally, Professor Elöd's argument that because the amounts of arginine and lysine in wool account only for 10 per cent. of its weight, they cannot provide an explanation of an isoelectric region between  $p_{\rm H}$  5 and 7 is inadmissible. For apart from these bases and the associated dicarboxylic acids, the remainder of the wool consists of non-reactive side chains to the main peptide chain, side chains which can play no part in reaction with acid and alkali. Actually, wool must be *expected* to have an isoelectric region if salt linkages between arginine and lysine, on the one hand, and aspartic and glutamic acids on the other hand, have a real existence in wool.

In reply to Miss Lloyd, I need hardly say that the wide range of

minimum swelling observed by her in the case of horse hair and silk gut has no parallel in the case of wool; and the argument for the existence of an isoelectric range with wool is not based, either directly or indirectly, on swelling measurements. The diminished capacity for swelling induced by drying in the case of gelatin gels and collagen fibres, has an interesting parallel in the effect of drying and dryingconditions on the water-adsorption capacity of wool. The higher the temperature at which wool is dried, the lower is its affinity for water, but the effect of drying is in all cases eliminated by exposure to saturated air or immersion in water. It is therefore improbable that peptide linkages are formed from salt linkages by drying, at least in the case of wool. We have, however, accumulated a certain amount of evidence which seems to show that peptide linkages may be formed from salt linkages when wool fibres are steamed in a state of strain, reminding one of the corresponding changes undergone by egg albumin during heat coagulation. It is possible that Miss Lloyd may find the answer to her enquiry in some linkage other than the salt linkage. We have, for example, been able to show by four distinct lines of evidence that the micelles of wool are attacked by water at temperatures above 45° C. The linkage (if any) which is opened seems to be unconnected with amino and carboxyl groups. A possibility which is receiving consideration in this connection is the oxygen linkage, and it is again interesting to recall that Lewis found it necessary to suggest a linkage of the ethylene oxide type to explain the phenomena of denaturation.

In reply to Dr. Bolam, I have to suggest that he is mistaken in attempting to apply, to wool, conclusions which are valid only for gelatin. The fact that the swelling and osmotic pressure of gelatin are smaller in sulphuric acid than in hydrochloric acid is very well known. Similarly, the existence of a common maximum of osmotic pressure for gelatin combined with monobasic acids appears also to be well established, except perhaps in the case of acetic acid. What Dr. Bolam has overlooked is the insoluble and rigid character of the wool fibre, in whose structure the free amino groups are widely separated. On purely structural grounds, the possibility of one sulphuric acid molecule combining with two amino groups is somewhat remote, so that sulphuric acid will tend to behave as a monobasic acid. In agreement with this deduction, the observed swelling of wool in sulphuric acid is sensibly the same as in hydrochloric acid at the same  $p_H$ . A number of peculiarities in the adsorption of sulphuric acid by wool may be explained in terms of the same hypothesis.

As regards Dr. Bolam's second point, I would remind him that wool behaves as a much weaker base than gelatin. With the latter, a maximum osmotic pressure is realised at  $p_{\rm H}$  3.4 or thereabouts, so that buffer phenomena can hardly be expected to play a large part in determining osmotic pressure and swelling. With wool, on the other hand, combination with acid is complete only at  $p_{\rm H}$  I (approx.), compared with  $p_{\rm H}$  2.3 in the case of gelatin. Thus buffer phenomena must be expected to play a far greater part in determining the swelling of wool in weak acids than is the case with gelatin, a deduction which is in agreement with observed results and the Procter-Wilson theory of swelling.

In reply to Professor Peters, the justification for our statement that "until recently, the possibility of salt linkages playing any significant part in protein structure was rejected" is to be found in statements such as the following: "Such bodies (internal salts of the substituted ammonium types), if they exist, would be hydrolysed in solution. "As indicated in the paper, modern views of the constitution of the zwitterion indicate that it is composed of strong acid and base, so that if our view is correct that the internal salts of wool are to be regarded as zwitterions, the apparent behaviour of wool as a weak base does not imply that the salt linkages are hydrolysed in water.

In replying to Professor Peters' second point, I would first mention that the postulated equivalence between the dicarboxylic acids of wool and its arginine, lysine, histidine and amide nitrogen content, is not peculiar to wool but has a parallel in the case of egg albumin. The recent analyses of Calvery 11 have yielded the following figures:—

			per	cent.				pe	r cent.
Arginine			٠.	5.05	Glutamic acid				13.96
Lysine .	-			3.90	Aspartic acid				6.07
Histidine				1.39	Hydroxyglutan	ic ac	$\operatorname{id}$		1.36
Ammonia.	_			1.30					_

and the acids and bases are equivalent to within 2 per cent. If Vickery's data (loc. cit.) are substituted for those of Calvery in the case of arginine, lysine and histidine, the error in equivalence is a little under 5 per cent. It seems probable, therefore, that salt linkages between peptide chains play an important part in the constitution of egg albumin, and there is no difficulty in explaining the loss of affinity for acid and alkali after heat coagulation in terms of the conversion of ionisable salt linkages into true peptide linkages.<sup>12</sup>

The preceding analogy supports the general argument of our paper. In addition, X-ray analysis of fibre structure at present demands that α-amino and carboxyl groups shall be bound into the long peptide chains, leaving terminal amino and carboxyl groups free to form internal salts, so that there is no possibility of explaining the action of acid and alkali on wool in terms of the  $\alpha$ -amino and carboxyl groups of a true zwitterion. I believe that the action of acid on wool represents the back titration of aspartic and glutamic acids which are normally in combination with arginine, lysine and histidine. The salt linkages function essentially as zwitterions, and in view of the fact that the positive and negative ions are non-diffusible, there need be no difficulty in explaining the discrepancy in the dissociation constants. As regards the danger of applying the dissociation constant of a group in solution to the same group embodied in a protein, I am in entire agreement with Professor Peters. It was for this reason that no special emphasis was given to the agreement between the calculated isoelectric points and the observed isoelectric region of wool.

D. J. Lloyd, Chemistry of the Proteins, Churchill, 1926, p. 77.
 Calvery, J. Biol. Chem., 94, 613, 1931-32. Revised data quoted by Vickery Biochem. J., 26, 1101, 1932.
 Hendrix and Wilson, J. Biol. Chem., 79, 389, 1928.

## THE ELECTRICAL RESISTANCE OF WOOL FIBRES.

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The investigation of the electrical resistance of wool in fibre form suggests the possibility of elucidation of facts concerning fibre structure. the mechanism of water absorption (since resistance varies with moisture content), and, finally, important applications of the facts deduced to practical phenomena in processing and utilisation of the fibre in bulk form. It is fully realised that the results obtained upon single fibres will not necessarily be wholly applicable to the material in yarn or fabric form, owing to the complicated structure of the latter, but nevertheless with suitable modification to meet bulk conditions many practical phenomena may be explained thus, such as e.g. electrification in the carding, spinning and weaving processes and secondly, the use of wool as an electrical insulator. Electrification in processing is evidently due to the high resistance of the wool preventing the rapid discharge of static electricity formed by friction. In practice, efforts are made to reduce such electrification by the application of water, weak soap solutions, and oil, and to eliminate it by maintenance of proper moisture conditions by artificial humidification of the atmosphere. The second practical application is the use of wool as an electrical insulator, where in addition to its high insulating powers, it has the great advantage of being non-inflammable.

The methods described in this paper refer to determinations of direct current resistance of wool fibres along their length. The present work is mainly concerned with the measurement of electrical resistance of single fibres, and presents a new method of attack on the fundamental problem of the wool fibre structure. The method is also applicable to any textile fibre or similar body having a high resistance. The field of work thus opened up is very broad, and the results presented here must, from this standpoint, be regarded largely as preliminary in nature.

#### Previous Work.

Previous work on the electrical resistance of single fibres was done by Slater. He measured the resistance of cotton fibres by the rate of discharge of an electroscope, the humidity being controlled by sulphuric acid solutions. The method only gave comparative results, though it could have been adapted to give absolute values, if it had been necessary.

Murphy and Walker 2 worked with both wool and cotton fibres, but used at least sixty in parallel to get a measurable deflection. methods of measurement were electromagnetic in principle, and they too used sulphuric acid solutions to give the desired humidities. Most

F. P. Slater, Proc. Roy. Soc., 96B, 181, 1924.
 E. Murphy, and A. C. Walker, J. Physic. Chem., 32, 1761, 1928.

of their work was concerned with yarns and insulated wires twisted together, and dealt largely with the subject of electrical insulation rather than with single fibres. It is to be classed with that of Evershed,3 Kujirai and Akahari,<sup>4</sup> and Curtis.<sup>5</sup> Reviews of the use of textiles for electrical insulation purposes have been published recently by Martin 6 and New.7

## Experimental.

## Method of Measuring Resistance.

The electrical resistance of single wool fibres may be as high as 10 15 ohms even at humidities of approximately 50 per cent. R.H., and therefore unless very large voltages are used the currents produced will be very small. In general laboratory practice, it is very inconvenient to use D.C. voltages of more than a few hundred volts, and therefore a method of measuring very small currents is essential. Throughout this work the method used by Townsend 8 for the measurement of ionisation currents has been adopted. In this method the current to be measured is balanced by an equal and opposite current produced by changing the potential difference of a fixed condenser at a definite rate. The rate is varied so that the needle of a Lindemann electrometer remains at its zero position.

Let V be the voltage applied to a fibre of resistance R ohms, then the current (or rate of change of charge) is V/R amperes. If C is the capacity of the condenser in farads and v the potential difference between its plates in volts, the charge on either plate is Cv coulombs. If v is changing, the rate of change of charge is  $C\frac{dv}{dt}$ . If these two rates are made equal and opposite

$$\frac{V}{R} = C \frac{dv}{dt}$$

$$R = V/C \frac{dv}{dt}.$$

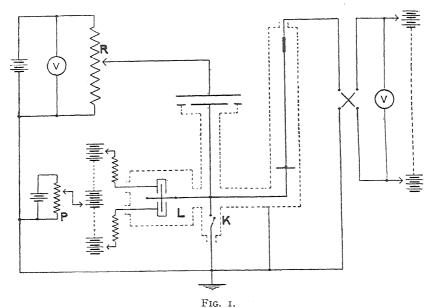
i.e.

If R is constant during an experiment,  $\frac{dv}{dt}$  is constant, and can be determined by timing the sliding of a potentiometer contact along a wire with a known potential drop along it. Hence the resistance of the fibre can be measured with an accuracy amply sufficient for the purposes required, since the quantities involved are easily determined. As the method is a null one, it is unnecessary to determine the sensitivity and capacity of the electrometer, but it is essential that its zero should remain constant. It is desirable, however, that the sensitivity should be as high as is convenient to give as great accuracy as possible, and to this end the capacity of the needle system must be made small. Similarly, the insulation resistance between the needle system and earth should be high, although, as this system is maintained at very nearly earth potential, the leakage can only be small.

<sup>&</sup>lt;sup>3</sup> S. Evershed, J. Inst. Elec. Eng., 52, 51, 1914. <sup>4</sup> Kujirai and Akahari, Sci. Papers, Inst. Phys. Chem. Res., 1, 94 (Tokyo), 1923. <sup>5</sup> H. L. Curtis, Bur. Stand. Bull., 11, 359, 1914-15.

R. I. Martin, J. Text. Inst., 32, P165, 1931.
 A. A. New, J. Soc. Dyers & Col., 47, 10, 1931.
 Townsend, Phil. Mag., 6, 598, 1903.

The circuit used is shown in Fig. 1. It will be noticed that the whole of the wiring connecting the needle, fibre and condenser, is earth shielded. In making a measurement the earthing key K is opened, and the time for the sliding contact of the rheostat R to move from end to end is timed, while the needle of the Lindemann electrometer L, observed microscopically, is kept at approximately its zero position. To render the timing more accurate a fiducial mark is chosen on the microscope eyepiece scale close to the zero or earthed position of the needle. When the needle passes this point the stop watch is started, and the contact of the rheostat is then moved so as to keep the needle on its original side of the mark. When the contact has reached its limiting position, the needle moves over the mark again and the watch is stopped. The times used vary from 20 to 300 seconds, an average being about 60 seconds. Less than 20 seconds is difficult to measure accurately, and when the time is over 300 seconds the error, due to leakage currents over the insulators, is appreciable. Owing to the range of times available, and also to the wide variations possible in



the two voltages and the capacity, this method can be used to measure a very large range of resistances very conveniently. In this work values from 10<sup>11</sup> to 10<sup>16</sup> ohms have been measured.

The voltages applied to the fibre vary from 3 to 300 volts, provided by H.T. dry batteries. The voltage range (v) for the condenser potentiometer (R) is generally 6 volts, but ranges from 2 to 12 volts. The Lindemann plates are maintained at  $\pm$  18 volts throughout. A potentiometer P is provided to bring the zero of the instrument to the same position with the plate voltages on as when the plates are earthed. This eliminates a possible source of variation in the zero of the electrometer.

The condenser has a plate 5.08 cms. in diameter, surrounded by a guard ring of 13 cms. outside diameter. The gap between them is only about 0.02 cms. The upper plate is supported by three small blocks of glass of equal thickness standing on the guard ring. The spacing generally used was 1.00 mm., giving a capacity of 1.80 10-11 farads. Some difficulty has been found in bringing the central condenser plate and the guard ring into exactly the same plane. This introduces a small error into the

calculated capacity of the condenser. By measuring the capacity with various blocks of glass it is possible to allow for this error with sufficient

accuracy,

Trouble was experienced in finding a suitable insulating material for the leads to the electrometer needle. Quartz was used at first, but was found to be unsatisfactory, especially at high humidities. Waxed quartz was better, but showed a charge absorption effect. Finally "Bank of England" sealing wax was found to be an excellent insulator, even at humidities as high as 90 per cent. For convenience quartz coated with the sealing wax was used. If a leak occurred, it could be eliminated by removing the insulator and gently reheating the sealing wax, taking precautions not to blacken it. In assembling the apparatus it was, of course, essential not to finger the insulators.

For convenience, the measuring circuits and the controls of the heating

and the stirrer motor are concentrated on to one switch-board.

## Control of Humidity and Temperature.

It was realised from the outset that in this work the humidity and temperature of the atmosphere in which the fibres were situated must be controlled. The construction of this part of the apparatus entailed considerable research and, whilst only the final form will be described in detail, the earlier forms may be reviewed briefly as a matter of interest. Throughout the present work, the humidity has been controlled by means of saturated salt solutions, thus avoiding the complications ensuing with sulphuric acid solutions, as with the latter some vapour or gas can be distinctly smelt, especially at high concentrations. The saturated salt solution has the advantage of an unchanging vapour pressure even when it has absorbed or given up moisture. A difficulty with their use is that no very reliable or extensive data about the relative humidities thus produced are available.

Tunstall, on the earlier part of this work, supported the fibre under observation horizontally between electrodes in a copper vessel, between the double walls of which water was circulated from a thermostat. The vessel contained a saturated solution of a suitable salt. In this way the temperature was controlled to about  $1/10^{\circ}$  C. and the relative humidity to within 1 per cent. This apparatus was discarded because of impossibility of distinction between electric current along the fibre and the leakage current over the insulators. It was found that some of the effects then exhibited were due to the insulators and not to the fibres.

In the next apparatus the fibre was vertical and enclosed in a glass flask immersed in a thermostat bath. The fibre carried a clip at its lower end, which was normally in contact with a metal plate. The fibre could, however, be raised, and thus allowed the insulation to be tested at any time. A saturated salt solution in the bottom of the flask controlled the humidity, but as no stirring of the air was provided equilibrium was reached very slowly.

An unsuccessful attempt was made to work with the fibre freely suspended in a similar way in a controlled temperature and humidity room. Opening of doors and the presence of an observer caused too violent changes in resistance. The fibre was then placed in an air-tight wooden box over a salt solution, and the air stirred by means of a fan driven by a motor outside the box. The temperature of the box was not regulated, but as it was kept in a thermostatically controlled room, it was expected that this would not be necessary. The results were encouraging but, as the tem-

<sup>&</sup>lt;sup>9</sup> Wool Industries Research Assocn., Private Pubn. No. 133.

perature control was unsatisfactory, the present apparatus was constructed.

## Present Apparatus.

As already outlined the main objects in designing the present apparatus were accurately to control the temperature, and hence the humidity, and to provide means whereby six fibres could be conditioned at once, and measurements made on any one of them. The general arrangement of the apparatus is shown in Fig. 2. It consisted of an "oven"  $43 \times 35 \times 30$  cms., to contain the fibres, surrounded by a water bath on all sides except one, which side had double doors. The inner doors were sealed at times, but this was found to be unnecessary.

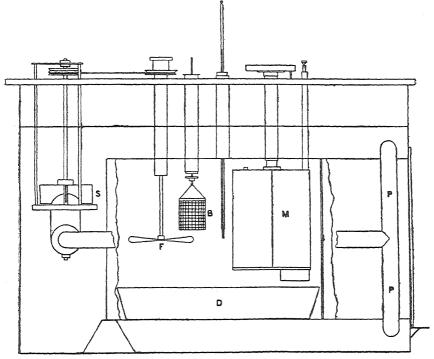


Fig. 2.

A pad of sponge rubber was placed against the inner doors to assist the thermal insulation.

The bath was heated electrically by four 250 watt radiator lamps (not shown in Fig. 2), at the left-hand side of the tank, connected to a series-parallel switch, which allowed the heating to be varied from 125 to 1000 watts as desired. The temperature was controlled by a mercury-toluene regulator (at the same end but also omitted from Fig. 2) through an Isenthal relay which controlled two lamps. A little glycerine was placed on top of the mercury surface to prevent the surface fouling, and to damp the vibration caused by the stirrer. The stirrer S was, in effect, a submerged centrifugal pump which drew water through holes in the pipe PP from the right-hand end of the tank, and delivered it into the left-hand end with a violent stirring action. The upper bearing of the pump

was a ball-bearing, and for the lower one ebonite on ebonite was used successfully. The whole of the water (about 90 litres) was circulated in  $2\frac{1}{2}$  minutes, and no variations in the temperature from point to point could be detected. The temperature of the air in the oven could be thus maintained easily to within  $\pm$  0.05° C., which was amply accurate enough for this purpose.

The saturated salt solution was contained in a photographic dish covering the whole of the floor of the oven. A circulation of air was maintained

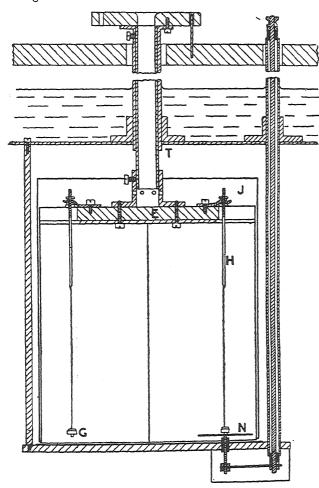


Fig. 3.

by a fan F inside the oven, driven from the stirrer. A clutch on the pulley allowed the fan to be stopped if necessary, but it was found that resistance measurements were unaffected by having it run-The ning. fan thermoshaft, meter, leads, etc., passed through tubes soldered into the roof of the oven. In each case care was taken to make the oven airtight.

For those experiments in which it was necessary to know the regain, i.e.the moisture content expressed as a percentage of the dry weight of the wool, a sample of wool, in an open form, was exposed in the wire basket B, hanging in the oven. This was attached to the arm of a balance by means of a rod passing up

one of the tubes, so that the weight of the wool could be determined at any time. At the end of the experiment the dry weight was found, so that the regain could be calculated. Except when the wool was being weighed, the basket was raised so that a plate above it made an airtight joint with the rubber washer attached to the lower end of the tube. During weighings, the fan was stopped and air leaks were largely prevented by a small aluminium disc, which was a very loose fit on the vertical rod from the basket, and similar to that used in the later forms of Joly's steam calorimeter.

Six fibres were suspended inside the oven simultaneously, and measurements could be made on any one of them at will. The fibre-holding mechanism M is shown in more detail in Fig. 3. Each fibre was threaded through a small hole in the end of a brass rod H and secured to the rod with secontine. The rods screwed through plates held by clips on an ebonite disc, which could be raised and rotated from outside the oven, and lowered at six appropriate positions, by the supporting tube T, which was a good fit into one of the tubes attached to the roof of the oven. Connections were made to the clips by six wires passing down the supporting tube T and through holes in which they were a good fit, thus preserving the airtightness of the apparatus. The six wires terminated at the upper end in two-way switches by means of which the H.T. connection could be made to any fibre, but if the fibre was not so connected, it was earthed. spring clip G was attached to the lower end of each fibre, and served to make contact with the plate N connected to the Lindemann electrometer needle, when the ebonite disc was lowered. It was found that a piece of aluminium foil between the jaws provides a better grip on the fibre. Between the fibres radial earth shields were provided. A cylindrical earth shield J surrounded the whole fibre mounting, and a circular disc provided shielding at the bottom. All these were made of open gauze or perforated metal in order to allow the circulation of air round the fibres. The plate N was supported by an insulator in the circular bottom shield, and the connection to the electrometer was made by an earth-shielded rod passing up a tube, as shown in the diagram.

The vibration caused by the stirrer greatly affected the Lindemann needle, and so the electrometer and the observing microscope were sup-

ported on a framework built out from a wall.

## Preparation of the Fibres.

Except where otherwise stated the fibres have been washed in three changes of benzene, distilled water, a dilute solution of saponin, and finally rinsed in distilled water. Care was taken not to finger the fibres when mounting them on the fibre holders.

The lengths were measured from their emergence from the hole in the holder to the point of gripping of the clip, to the nearest half millimetre. Their diameters were determined at 30-50 points along their length, by mounting the fibres with Canada Balsam in microscope slides, and measuring them in a projection microscope with a magnification of 1000. Some of these readings have been compared with those obtained on the "Rotator", 10 which allows ellipticity to be determined. The agreement was good enough to allow the simpler microscope method to be used for general work. When it was desired to select particularly regular fibres for an experiment, these were examined in the Rotator so that any showing marked ellipticity or other irregularities could be discarded.

#### Results.

#### Change of Resistance with Time.

Measurements on numerous fibres have shown that no generalisation can be made as to the time required for a fibre to reach hygroscopic equilibrium with the atmosphere in which it is placed. Primarily, about eighteen hours was allowed for conditioning, but this was shown later to be insufficient and finally results were taken after a minimum

<sup>&</sup>lt;sup>10</sup> S. G. Barker and M. H. Norris, J. Sci. Inst., 7, 22, 1930.

interval of three days, provided that the change in resistance from day to day was only a few per cent. At any time after the first few hours successive measurements showed that the resistance had a definite value, but on repeating the measurements at intervals of say four hours, changes could be observed. The changes were due to two causes; the approach of the fibre to an equilibrium resistance or to hour-to-hour fluctuations.

These fluctuations of from 5-10 per cent., or possibly more, caused a good deal of concern, and many attempts were made to eliminate them. The fibres were generally placed in distilled water immediately before mounting and exposure to the controlled humidity. Similar fluctuations were observed, however, when the fibres, after mounting, were subjected to a very low humidity before being placed in the apparatus. The direction of approach to the equilibrium resistance had seemingly no effect on the fluctuations.

In some cases all six fibres showed the same variation, thus creating strong suspicion as to the constancy of the humidity or temperature. In other more frequent cases, however, some fibres showed fluctuations while others remained steady. It is known that the moisture content of a single fibre, as determined by gravimetric methods, reaches equilibrium with the atmosphere in a few minutes, so that the fluctuations now found may be due to some internal processes of readjustment within the fibre affecting the distribution of the water contained. If this is the case, then the electrical resistance method, since it is so sensitive, should prove valuable in studying such phenomena.

This variation of resistance with time was the limiting factor in the accuracy of the experiments, since all the quantities involved in the measurement could be determined accurately. For most fibres the error would probably be within 5 per cent. but, owing to difficulties in measuring up fibres dimensionally, the specific resistances may be in error by about 10-15 per cent. These errors are not so important as they might appear when compared with the variation of 20-30 per cent. for a change of I per cent. in the relative humidity. In the present work, where comparisons have been made, the fibres compared have been placed in the apparatus together, and thus measured under identical conditions.

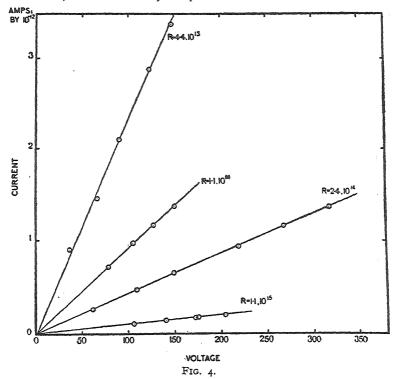
#### Resistance and Voltage.

The earliest experiments showed that the resistance of a wool fibre was independent of the voltage and polarity. Further, there was in general no change of resistance with time. The only exception to this was that with some fibres of exceedingly high resistance, the resistance apparently decreased at first but reached a steady value in a few minutes; an opposite effect to that which would have been produced by polarisation, and which may have been due to a slow charging up of the fibre. This question is to be investigated further. In all other cases wool fibres behaved exactly like a normal conductor of high resistance over the range of voltage and humidity used (0-300 volts, 50-85 per cent. R.H.). Typical curves are given in Fig. 4.

The fact that a wool fibre generally obeys Ohm's Law is interesting. Other workers on the resistance of fibrous insulators have found that the resistance decreases with increased voltage. Evershed <sup>3</sup> explains this as being largely due to endosmose, and Murphy and Walker <sup>11</sup> as being

<sup>&</sup>lt;sup>11</sup> E. Murphy and A. C. Walker, J. Physic. Chem., 33, 509, 1929.

connected with electrolytic conduction. Similar effects are found by Curtis,<sup>5</sup> and Kujirai and Akahari,<sup>4</sup> with hygroscopic insulators. Since these workers used yarns mainly, the effects might be due to the more complicated structure as compared with a single fibre. Slater, however, finds the same thing with single cotton fibres. It may be mentioned that Evershed found that fibrous insulators, when sensibly wet, obeyed Ohm's Law, but this is hardly comparable with the results obtained here



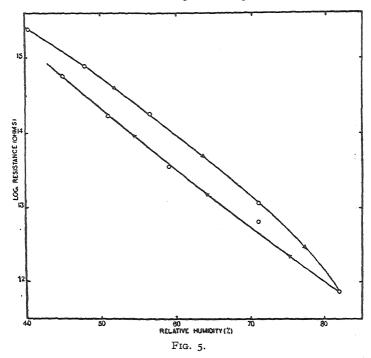
for comparatively low humidities. Most of these workers, too, find a change of resistance with time of application of voltage, which they attribute to endosmose, absorption currents, or electrode reactions.

It is suggested that, in the present work, the reason for the adherence of wool fibres to Ohm's Law is that very small current densities have been used throughout.

#### Relationship Between Resistance and Relative Humidity.

From preliminary experiments it was found that the resistance was very sensitive to small changes in the humidity of the atmosphere, with which it was in equilibrium. It was noticed that there was a marked hysteresis effect in the resistance-relative humidity relationship. There was a similar but smaller hysteresis effect in the relative humidity-moisture content relationship for wool, which suggested that there might be a simpler relationship between resistance and moisture content. Fig. 5. shows the general type of curve obtained when the humidity is varied cyclically. For this experiment a form of apparatus was used

in which the dew-point could be determined. In this experiment the fibre had been taken round several cycles, beginning at a low humidity, and at the end of each cycle was left over solid calcium chloride (R.H. about 3 per cent.). The curves obtained for different cycles were not coincident, but they had the same general shape after the first half cycle.



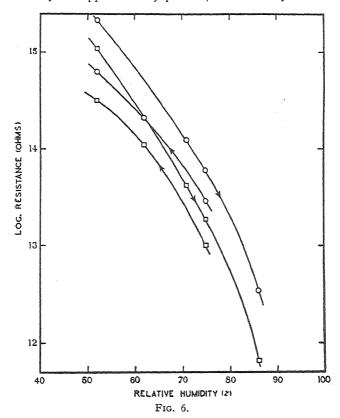
This irregularity in the first half cycle was also observed in later experiments. It will be noticed that for a humidity range of 40-82 per cent. the resistance increases eight or nine times for a 10 per cent. decrease in the relative humidity. The maximum humidity at which experiments could be made was 90 per cent., but at this humidity measurements were unreliable, owing to leakage over the insulators.

## Relationship Between Fibre Type and Humidity Effects.

An experiment was performed to determine whether fibres from two wools of very different types were equally affected by changes in the relative humidity. The wools chosen were Welsh wool (high sulphur content) and Romney Corriedale (low sulphur content and of a more hairy nature). Three fibres from similarly cleaned samples of each wool were selected, and mounted in the apparatus. The fibres were subjected to a cycle of humidities ranging from 3 per cent. to approximately 100 per cent., measurements being made over the range 52-86 per cent. Obermiller's 12 data for the various salt solutions, or previous dew-point measurements, were used for humidity determinations. Only comparative results were required. Fig. 6 shows the curves obtained for two of

<sup>12</sup> Obermiller, Z. physik. Chem., 109, 145, 1924.

the fibres. Comparing the two curves for increasing humidities, it is seen that they are approximately parallel, and similarly for the curves



for decreasing humidities, although the two curves referring to one fibre are of rather different slopes. The effects, therefore, of humidity on the two types of fibre were similar in character.

# Relationship Between Resistance and Percentage Moisture Content (Regain).

To determine the regain of the fibres a sample of wool (about I gm.) suspended in the apparatus was weighed at the various humidities, and at the end of the experiment its dry weight was determined. Thus the regains were known at the various humidities at which resistance measurements were made. In general the relative humidity was changed overnight, and the resistances of the fibres and weight of the sample measured the following day. The latter was found to be sensibly constant throughout the day.

Two sets of experiments were carried out. In the first set the regain was not allowed to go outside the range in which it was possible to measure the resistance. These results, plotted on a logarithmic scale, gave the type of curve shown in Fig. 7. In the other set the fibres were exposed to a saturated atmosphere after the readings at the highest regain

were completed. When the humidity was brought back to its previous high value there was a marked difference in resistance as indicated by

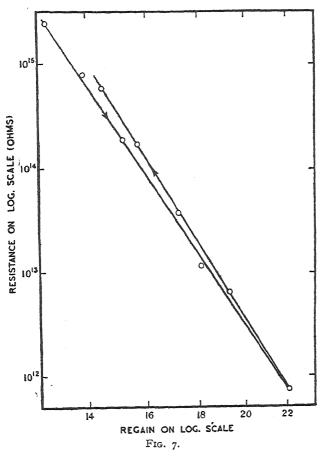


Fig. 8, in which both scales are logarithagain mic. From both Figs. 7 and 8 it that appears there is approximately linear relationship between the logarithm of the resistance and the logarithm of the regain, over the range of regains from II-I7 per cent. apparent deviation from linear relationship at higher humidities, shown by all the fibres in the second experiment, might be due to experimental errors in the weight determination.

It is interesting to note that the slopes of the straight portions of the

lines representing the log resistance/log regain relationship for all the fibres used are the same to within the limits of experimental error, and have a mean value of — 15.0. For all these fibres, over the region of humidities considered, it is, therefore, possible to write

$$\log R = -15.0 \log M + C, R = C'M - 15.0,$$

where M is the regain, R the resistance in ohms, and C and C' are constants dependent on the particular fibre.

or

Murphy and Walker, 11 using wool threads, obtained an expression

$$R = C'M - 16.4$$

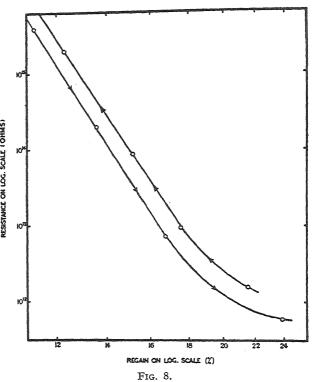
They found apparently that the points obtained for increasing and decreasing regains all lay on one straight line, instead of on two parallel lines as found in this work. This might account for the greater slope of their lines. Considering also that Schloesing's <sup>18</sup> data were accepted for

<sup>&</sup>lt;sup>13</sup> T. Schloesing, Bull. Soc. encour. indust. nat., 8, 717, 1893.

the values of the regain corresponding to various humidities, the results are in good agreement with the present work. The fact that probably

insufficient time was allowed for conditioning does not invalidate these observed hysteresis effects, since a longer time for conditioning would be expected to in- 5 crease observed crease observed gdifferences be- 3 tween the maximum resistances was regain, or for a fixed humidity.

The upward bend of the resistance-regain curve shown in some cases at high humidities may correspond to the effect found by Speakman 14 in studying rigid-



ity. He finds a bend in the rigidity-regain curve and explains this as being due to the water added above this value simply flooding the large pores of the wool. This would rather imply that the water spaces in wool can be divided into small and large with a fairly sharp division between them.

## The Effects of Electrolytes and Oil.

The resistance of fibrous insulators is known to be dependent on the quantity of electrolyte they contain. Murphy and Walker <sup>2</sup> find an increase of fifty times in the resistance of raw cotton on washing. Similarly the resistance of silk is increased by washing in neutral water and still further if made isoelectric. <sup>15</sup>

Wool fibres were selected from a previously cleaned sample of 56's drycombed top and rewashed in tap, distilled, and conductivity water respectively. Their resistances were then measured under the same conditions, and it was found that the specific resistances of those washed in distilled and conductivity water were no higher than those washed in tap water.

J. B. Speakman, Proc. Roy. Soc., 132A, 167, 1931.
 British Silk Research Association. Privately communicated.

These results suggested that it would be interesting to know the effect of soaking fibres in sodium chloride solutions of known strength. Some fibres were allowed to soak for three and five days respectively in salt solutions of various strengths. After soaking, the fibres were rapidly washed in two changes of distilled water and their resistances compared with those of untreated fibres. The concentrations of the solutions used varied from 125 gms. to 360 gms. per litre, the latter giving a saturated solution. The resistances of the fibres were reduced by amounts varying from 6 to 150 times, depending on the strength of the solution and the time of immersion. The decrease in resistance was much more marked in the experiment where the fibres had soaked for five days, suggesting that the period of three days was insufficient for the sodium chloride to penetrate the fibres.

Some fibres were also mounted straight from the salt solution without any washing, but their resistances were much too low to be measured by this method.

Although there was a marked decrease in resistance on soaking in the sodium chloride solutions, the specific resistance was still very much higher than the resistance of the solutions (about 10<sup>7</sup> compared with 20), showing that a very small fraction of the ions was available for conduction. The fibres still obeyed Ohm's Law and no polarisation was detected.

A comparison of resistance was made between fibres from commercially clean combed wool, similar fibres washed in distilled water, and fibres washed in benzene and distilled water. It was found that the washing in water had the effect of increasing the specific resistance about eight times, while the removal of the oil  $(\frac{1}{2},\frac{3}{4})$  per cent. olive oil) had no influence on the resistance. This was of some technical interest, but need not be discussed further here. The following table gives some of the actual results obtained in this section of the work:—

Treatment of Fibres.	Specific Resistance in megohms-cms., at 75 Per Cent. R.H. and 25° C.						
Washed in tap water		240 220	210 200	260 — 240	400 — 300	230 — 220	_
Washed in distilled water NaCl 2·14N. 3 days; washed rapidly NaCl 4·28N. 3 days; washed rapidly NaCl 2·7N. 5 days; washed rapidly NaCl 5·4N. 5 days; washed rapidly		350 63 37	340 61 43 —	220 — — II·5 I·77			
Washed in benzene and distilled water Washed in distilled water only . Untreated	•	220 230 43	250 230 36	240 240 58	290 28	220 — 36	200 — 34

From these results it is evident that some electrolyte in solution can be fixed or adsorbed by the wool. If the amount of electrolyte is excessive, this process is insufficient and some electrolyte is left for ionic conduction, although it is only a very small fraction of the total present in the fibre.

## Effect of Steaming.

Long even fibres were chosen and divided into two or three portions. Portion (a) was placed in distilled water, portion (b) was steamed tensionless for half-an-hour, and portion (c) was steamed taut for half-an-hour. After steaming, portions (b) and (c) were placed in distilled water, and then all three portions were mounted and placed over sodium chloride solution. The table given later shows that the specific resistance is unaffected by steaming free from tension, but that it is increased by about 60 per cent. by steaming under slight tension. The tension was due to the weight of the suspended fibre clip, and was of the order of  $3 \times 10^4$  gms. per square centimetre.

The experimental method described above ensured that the portions of a particular fibre should all have the same electrolytic content, since they were all immersed in the same distilled water before mounting. It was also desired to see if steaming had any scouring action on the fibres, so some experiments were made in which the steamed portions were mounted directly after steaming, the untreated portion being immersed in distilled water as before. It was found that there was no scouring action, the resistance being, as before, unaffected by steaming when the fibre was free from tension, but increased when the fibre was subjected to a slight tension.

A table of specific resistances of fibres steamed tensionless and taut is given below:—

Treatment of Part.	Specific R	Specific Resistance in megohms-cms., at 75 Per Cent. R.H. and 25° C.								
	Fibre 1.	Fibre 2.	Fibre 3.	Fibre 4.	Fibre 5.	Fibre 6.				
Not steamed Steamed tensionless	121 126 —	77 77	57 63 98	39 57	46 67	35 57				

## The Effect of Stretching and Steaming Fibres.

It was not found possible to measure the resistance of stretched fibres while under tension, owing to the difficulties of insulating satisfactorily the stretching apparatus, and also due to the fact that there would be considerable plastic flow of the fibre while it was conditioning, thus bringing about a change in the stresses involved. It was for this reason that steaming was resorted to, so as to give the fibre a permanent set. This, however, complicated the interpretation of the results, since steaming is known to have a definite action on the molecular formation of wool keratin when in the stretched state.

Long regular fibres were selected and divided into two portions. One portion was untreated, while the second portion was stretched under water and then steamed for half-an-hour. The fibre was stretched on a frame which could be placed bodily in the steam chamber. Before mounting, both portions were placed in distilled water so as to equalise their electrolytic content. The extensions used varied from 10 to 57 per cent., but were mostly about 30 per cent. The stretched fibres had a very much higher specific resistance than the unstretched ones, but there appeared to be no relationship between the increase in resistance and percentage extension, as will be seen from the following table:—

Treatment.	Specific Resistance in megohms-cms., at 75 Per Cent. R.H. and 25° C.								
Unstretched		270 1920 — —	220 740 — —	17·6 — 102 —	32 — — 230 —	35 — 220 —	39 — — — 135	46 — — 257	

These results have been confirmed by measurements made on fibres extracted from yarn which had been stretched and steamed on a commercial scale in a special machine. The yarn was increased in length by about 30 per cent., but it does not follow that all fibres would have received the same extension. The following table shows the specific resistances of fibres taken from the unstretched and stretched yarn:—

Fibres from—	Specific Resistance in megohms-cms., at 75 Per Cent. R.H. and 25° C.							
Unstretched yarn		52,	64			33,	20	
Stretched yarn .		370,	390,	290,	550	242,	230,	286

These changes in resistance due to steaming and stretching may be mainly due to changes in the regain of the fibres, so it is interesting to compare them with the results of A. T. King <sup>16</sup> on the regain of stretched fibres. Working also with single fibres (R.H. 70 per cent. and regain 15 per cent.) he found that for fibres stretched dry there was an increase in weight of about 1.5 per cent., while for stretched and steamed fibres the weight decreased on an average by about 0.8 per cent. For fibres steamed slack an average increase in weight of 0.6 per cent. was obtained. These results are explained as being due to changes in the porosity of the fibre.

Considering first the results for fibres which were steamed slack, it has been shown that there is no change in the electrical resistance due to simple steaming. The small increase in weight obtained was only just outside the limits of experimental error, and it is probable that the alteration in regain due to steaming is negligible.

The increase in resistance, about 60 per cent., brought about by steaming while subjected to a slight tension, is probably due to a small decrease in the regain. This decrease would only have to be about 0.5 per cent. to give the required 60 per cent. increase in resistance, and so is approximately equal to the decrease observed by King for fibres which had been given a permanent set of about 30 per cent. There is microscopic evidence that this decrease in regain is due to the pores being distorted by the stretching force, and becoming sealed up under the action of the steam. It seems possible that slight distortion and consequent sealing up of the pores may occur when the fibre is steamed under a slight tension such as that due to a fibre clip, but no direct experimental evidence on this point has been obtained in the present work.

The large increase in resistance obtained on giving a fibre a permanent set with an extension of about 30 per cent. cannot be due solely to a

decrease in regain since, as already mentioned, the decrease in regain, 0.8 per cent. approximately, would only give a change of the order observed for fibres steamed under very slight tension. Hence it is probable that the change in resistance on stretching may be due to changes in the configuration of the water paths, in which, as will be shown later, the conduction probably occurs, or alternatively may be

partially due to changes in fibre structure.

Recent X-ray work on wool fibres by Astbury and Street <sup>17</sup> has shown that when a wool fibre is stretched by more than 30 per cent. a change in the molecular structure of the keratin occurs. More recent work by Astbury, the results of which have been communicated privately, shows that the modified or extended form takes up water in a way which differs from that of the normal form. This is confirmed by Norris <sup>18</sup> on the swelling of wool, who shows that a stretched fibre swells in caustic soda more than an unstretched fibre. It is clear therefore that the distribution of water is different in a stretched and unstretched fibre. The present work suggests that the stretching results in a decrease in water available for conduction, and it therefore seems to be in agreement with Astbury's results that when a fibre is stretched, the water is taken up by the wool substance in a more intimate manner.

The change of resistance of wool is noticeable at extensions less than 30 per cent., while the change in X-ray structure begins at about 30 per cent. extension. This, with many other points, needs elucidation.

## Other Results.

By using thick and thin fibres from the same wool, an attempt was made to see if the resistance was a surface or volume effect. The results were not conclusive owing, no doubt, to the difference between the fibres, but the evidence tended to show that the resistance is a volume characteristic and not a surface one.

Several sets of fibres from wools of different sulphur contents were measured up, but no definite relation between sulphur content and specific resistance was found. Those with the highest sulphur content tended, however, to have high specific resistances. (The sulphur contents of the samples were kindly determined by Mr. J. Barritt.)

#### Discussion of Results.

## Electrical Resistance Phenomena as Indicators of Fibre Structure.

It is proposed to discuss the results from the point of view of their bearing on the structure of the wool fibre, without undue elaboration of the theory being attempted.

There is very little reason to think that, in hygroscopic fibres such as wool, there is any appreciable conduction through the colloidal substance of the fibre, since this has a resistance when dry which is very high compared with the purest conductivity water. Speakman <sup>14</sup> states that the micelles in a wool fibre are relatively if not entirely impervious to water. If the micelles were entirely impervious, it is clear that all conduction must take place in the water channels. Speakman shows later in the same paper that the micelles do absorb water to a small extent and there is other experimental evidence in

W. T. Astbury and A. Street, Phil. Trans., 230A, 75, 1931.
 M. H. Norris, Trans. Far. Soc., 28, 618, 1932.

support of this view. The specific resistance of the colloidal component of wool will, however, always be large compared with that of water, and, therefore, for the present discussion it will be assumed that the path of the current is entirely in the water contained in the fibre. This assumption has been made by all previous workers on this subject and, up to the present, there is no experimental evidence to the contrary.

In this work for the first time the specific resistance of wool at various regains and in equilibrium with atmospheres of various humidities has been measured. Typical values of the specific resistance of a fibre, which has been washed in distilled water, are given in the following table, together with the corresponding humidities and regains. Similar figures could be given for a large number of different fibres but all show the same trend:—

Relative Humidity.	Regain.	Specific Resistance.				
(Per Cent.)	(Per Cent.)	(Ohms — cms.)				
53	12	1.6 × 108				
63	14	1.5 × 108				
71	16	2.3 × 107				
79	18	6.0 × 106				
83	20	2.5 × 106				
86	22	1.3 × 106				

These specific resistances may be compared with that of conductivity water as usually prepared which is in the neighbourhood of 106 ohmscms.

Two points emerge immediately from these figures and need an explanation based on the internal structure of the fibre. The first is the high resistance of wool at medium humidities compared with the water it contains. The second is the very rapid change of resistance with regain, and with the relative humidity of the atmosphere with which the fibre is in equilibrium.

Considering the results given above for 12 per cent. regain, it will be seen that although water constitutes one-ninth of the fibre by weight. the resistance is 1600 times the resistance of a column of conductivity water equal in size and shape to the fibre. This means that if only I/I80th of the water were present even in a very pure condition distributed along the fibre with a uniform cross-section, the resistance of the fibre would be the same. Murphy and Walker 19 have elaborated a suggestion made by Evershed 3 to explain such facts, to the effect that the water in a hygroscopic insulator is contained in channels of very widely varying cross-section. The smaller the cross-section the higher the resistance per unit length, and consequently it is the constricted parts of the channels which determine the resistance. There may therefore be a relatively large amount of water contained in the larger spaces which adds very little to the resistance of the fibre. If conduction through the colloidal substance be ruled out, this seems to be a reasonable explanation of the facts based on very simple ideas. It is possible to formulate other theories to explain the reason why all this water is not available for conduction but they will of necessity be more complicated. The simple conception of conduction in the water channels will be followed up here.

<sup>&</sup>lt;sup>19</sup> C. Murphy and A. C. Walker, J. Physic. Chem., 33, 200, 1929.

The rapid variation of resistance with regain and relative humidity needs further consideration. It could be due to rapid changes in the dimensions of the constricted parts of the water channels. Speakman calculates that the intermicellar space changes from 6 Å to 41 Å between 0 and 100 per cent. R.H. This is of much too small an order to explain the resistance changes.

It is very difficult to conceive of any channel in a wool fibre changing its dimensions at the rate required by the resistance phenomena. In the typical figures given above, for example, the resistance increases about ten times for a decrease in regain from 14-12 per cent. The change in size of the water spaces cannot therefore be taken to

explain the changes in resistance as regain changes.

A much more reasonable hypothesis seems to be the breaking down of water paths as the regain of a fibre is decreased. For a consideration of this it is necessary to review briefly the question of pores in wool and hair fibres. This matter has been investigated by three workers in the last ten years from different aspects, and the general results are concordant, and therefore worthy of attention. Fisher <sup>20</sup> has approached the subject by studying the rate of evaporation of water from wool. Whipple <sup>21</sup> has explained the expansion and contraction of hairs with variations of the humidity as in the hair hygrometer, on the pore theory, while Hedges <sup>22</sup> has studied the question from the point of view of the heat of wetting of wool. Hedges' results for pore sizes are of the same order as those found by Speakman for intermicellar distances, indicating that the pores may be really the spaces between the micelles.

The pore hypothesis as stated by Fisher is that "the absorption of moisture (or other liquid) by wool or cotton is due primarily (not necessarily entirely) to a filling up of innumerable very fine pores of varying shapes and diameters, and that the vapour pressures of the wool-water systems, which are known to vary with the water content, are determined by the diameters of the pores that are full of water under the particular conditions." The original idea of pores seems to have been that they started from the surface and penetrated into the fibre. From the present work it is suggested that the water channels may be supposed to behave in the same way as the pores, and this suggestion has some support from a footnote in Fisher's paper. He says: "Such pores are not necessarily of uniform bore nor even of constant diameter in the same cross-section. A relatively long slit, for example, with a cross-section tapering sharply to the two ends (like a section of a double convex lens), might conceivably 'empty' first in the centre, leaving two water wedges at the ends."

This "emptying" of the wider sections of the water channels as the regain diminishes would cause the resistance of that channel to become practically infinite. Also, since the wider channels have the lower resistance the breaking down of these will cause a great increase in the total resistance of the fibre as the narrowed and therefore higher resistance ones are left. There will also be the general decrease in size of water spaces indicated by Speakman, which will have a contributory effect, but the breakdown of the channels must be much more important.

It is felt that these ideas, though perhaps elementary, may throw some light on the absorption of water by colloids such as wool. The

E. A. Fisher, Proc. Roy. Soc., 103A, 139, 1923.
 F. J. W. Whipple, Physic. Soc. Discussion on Hygrometry, 50, 1921.
 J. J. Hedges, Trans. Far. Soc., 22, 178, 1926.

form of the resistance-regain curve will depend on the statistical distribution of the sizes of channels, measured at their widest parts in the fibre.

## Summary.

An experimental method for measuring the specific resistance of wool fibres is described.

Results, mainly of theoretical interest, are given on the effect of various factors on the resistance.

It is suggested that longitudinal conduction in the fibre takes place through water paths of varying cross-section. The great increase in the resistance for a small decrease in regain can then be explained on the assumption that the water channels break down, those of greatest cross-section breaking down first and at their widest points, *i.e.* these paths are supposed to behave in the same way as the pores considered by previous workers.

## GENERAL DISCUSSION.

Dr. J. B. O'Sullivan (Manchester) said: An alternative possible explanation of the great change of electrical resistance of textiles with

change of moisture content may be given as follows.

The authors suggest that electrical conduction in wool takes place through pores. A similar view has been put forward in the case of cotton, particularly by Murphy. If we assume the validity of the Kelvin equation in such cases we can calculate the effective capillary radius of the pores from the published data for the water vapour pressure of cotton of various moisture contents. We thus obtain values ranging from about 10 to 1000 Ångström units.

It has been shown by the present authors and others that conduction in cotton and wool is mainly electrolytic. Now, since most ions are hydrated, and, therefore, carry with them an atmosphere of water molecules, we should expect them to experience a resistance proportional to the viscosity of the liquid through which they migrate. In capillary tubes, the viscous hindrance is proportional to the fourth power of the radius, and if this relation holds down to radii of the values stated above, we might expect the electrical resistance to change 108 fold.

This is amply sufficient to account for the recorded variation of resistance with moisture content. In fact it is more than sufficient. The difference may be due to the pores having a periodically constricted form, as suggested by the present authors, the effect of the constrictions on the electrical resistance being greater at low than at high moisture contents.

Mr. E. G. Cox (Birmingham) said: The hysteresis effect observed in measuring the resistance of wool fibres as a function of humidity is paralleled by the similar effect obtained in determining the adsorption isotherm of cellulose fibres under varying humidity. The experiments of Filby and Maass <sup>1</sup> indicate that the first 4 per cent. of water taken up by the fibre is adsorbed (i.e., it loses the characteristics of normal water) while the remainder is simply absorbed into the inter-micellar spaces. During the determination of the adsorption isotherm with decreasing humidity, the adsorbed water exerts less than the normal vapour pressure, thus causing the "hysteresis" effect. This, coupled with the

<sup>&</sup>lt;sup>1</sup> Can. J. Research, 162, 1932.

work of McBain, who has shown that adsorbed films possess enhanced conductivity, would seem to offer the basis of an explanation for some

of the results of the present paper.

Dr. J. R. Katz (Amsterdam) said: The measurement of the electrical conductivity of fibrous substances as a function of the degree of swelling (of the water content) of the fibres presents a good deal of interest for the theory of swelling. In a 2 per cent. gelatin gel conductivity is practically as large as in pure water, in very dry substances of this kind it is extremely small. How the water is distributed and bound between the micellae of a swollen body must find some elucidation by the way the electrical conductivity changes with the degree of swelling. This method may prove particularly interesting for a closer study of the orientation of the water molecules on the surface of the micellae, the existence of which is indicated by the diminution of entropy in swelling.<sup>2</sup>

It will then be advisable to use artificial fibres with different degrees of orientation of the micellae, as in natural fibres the structure is much

more complex.

Mr. Marsh, in reply, said: Dr. O'Sullivan's suggestion is very interesting and worthy of very careful consideration. We are now engaged in measuring the temperature coefficient of the resistance of wool fibres. This work should throw considerable light on this suggestion since, if it is correct, the temperature coefficient of resistance should be very simply related to the temperature coefficient of the viscosity of water. At present we have not enough results to come to any definite conclusion.

The hysteresis effect in the absorption of water by wool and similar fibres, referred to by Mr. Cox, is evidenced in many studies of the physical properties of fibres. In this electrical resistance work, however, we have shown there is a further hysteresis effect, viz., for a given moisture content the resistance is greater for increasing than for decreasing moisture contents. This can be readily seen from Figs. 7 and 8 in the paper.

I agree with Dr. Katz that the electrical resistance method has distinct possibilities in the study of water absorption in colloidal material. Owing to its great sensitivity, it may be of use in detecting and measuring effects which are too small to be dealt with otherwise.

<sup>2</sup> See my paper on the "Laws of Swelling," under paragraph 9, page 287.

## SOME PROBLEMS IN THE X-RAY ANALYSIS OF THE STRUCTURE OF ANIMAL HAIRS AND OTHER PROTEIN FIBRES.

By W. T. ASTBURY.

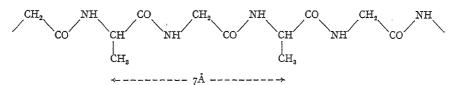
(Textile Physics Laboratory, The University, Leeds.)

#### The Structure of the Keratins.

The primary aim of crystallography, as developed by the methods of X-ray analysis, is the interpretation of chemical formulæ in terms of the actual three-dimensional arrangement of atoms and molecules: it therefore provides a general framework for the study of the solid state

and is the structural basis of modern stereo-chemistry. Great strides have been made in this field since the war, in many cases through direct and frequently unequivocal combination of diffraction and geometrical theory, and in other, and more complex, cases through reasoning arising out of the consideration of known physical and chemical properties in the light of X-ray analytical results which are themselves incomplete or ill-defined. In the latter class of problem the X-ray evidence, possibly —as yet—unintelligible in itself, can often establish firmly an explanation made plausible or probable on other grounds, or even provide just the clue required for the correlation of a whole mass of apparently unrelated phenomena. Perhaps in no branch of structural research is this valuable function of X-ray analysis more strikingly exemplified than in the study of vegetable and animal fibres. The progress that has been made through the linking-up of the chemistry of cellulose and its derivatives with their X-ray diffraction diagrams is really remarkable, while even in such a bewildering subject as that of the constitution of the proteins conclusions may now be drawn from the results of X-ray examination which permit us to catch glimpses of underlying common features of hopeful simplicity. It is particularly with these latter that the present paper deals. One cannot be dogmatic at this stage, but already there is no doubt that the outlook has grown so much clearer that it may prove helpful now to try to see just where we stand.

X-ray photographs of natural fibres show that the fibre substance is in most cases certainly crystalline, though often very imperfectly so, and that the submicroscopic crystalline particles, which have been identified with Nägeli's "micelles," are much longer than they are thick and lie with their common long dimension roughly parallel to the fibre axis or arranged spirally at a roughly constant angle to it. The diffraction diagram of cellulose fibres is also sufficiently complete to allow of the determination of the size of the molecular unit of pattern, so that by correlation of the whole of the X-ray data with our knowledge of the chemistry of the sugars and polysaccharides 2 we may now feel confident that the cellulose molecule is indeed a long chain of glucose residues and that the lateral cohesion of such chains is the structural basis of the cellulose crystallites which build up the substance of the natural fibres.<sup>1</sup> Natural silk,3 which is formed from the protein fibroin, does not give such a rich "fibre photograph" as that of cellulose, but Meyer and Mark 4, 1 applied to it the principles learnt from the latter and suggested that the fibroin crystallites, too, were no other than bundles of long molecular chains, but in this case polypeptide chains built for the most part of alternating glycine and alanine residues, thus:-



<sup>&</sup>lt;sup>1</sup> See, for example, K. H. Meyer and H. Mark, Der Aufbau der hochpolymeren organischen Naturstoffe, Leipzig, 1930; also W. T. Astbury, "The Structure of Fibres," Annual Reports of the Chem. Soc., 1931, Vol. 28.

<sup>2</sup> W. N. Haworth, The Constitution of Sugars, London, 1929.

<sup>3</sup> R. Feill (Annual Processing Constitution)

R. Brill, Annalen, 434, 204, 1923; O. Kratky, Z. physikal. Chem., 5B, 297, 1929; O. Kratky and S. Kuriyama, ibid., 11, 363, 1931.
 K. H. Meyer and H. Mark, Ber., 61, 1932, 1928.

But this interpretation of the fibroin photograph as the diffraction pattern of the simple polypeptide chains postulated by Fischer found no direct support in the X-ray photographs of other proteins, such as collagen, hair, muscle, etc., and it was not until the discovery of the reversible transformation of hair keratin 5 that the idea became convincing that proteins could exist and be photographed under certain conditions as extended polypeptide chains. It was found that the X-ray photograph of unstretched wool or hair was replaced by another, and quite different, fibre photograph when the hair was stretched, and that though the photograph of the unstretched fibre could not be explained in terms of the theory put forward for silk, the photograph of the stretched fibre actually was analogous to that of silk—which is always fundamentally the same, whether the silk is unstretched or stretched—and could be explained still more reasonably as arising from fully extended polypeptide chains,6 because hair is a fibre which is elastic over a great range. Even in cold water wool or hair can be stretched by as much as about 70 per cent., and it recovers its initial unstretched length exactly when the tension is released and the fibre is kept wet. When the initial length is regained, the normal photograph reappears: the processes of stretching and relaxation, accompanied by the corresponding changes from one fibre photograph to the other, may be repeated indefinitely. It is clear that we are dealing with a reversible transformation of the keratin molecule or complex, and that the ordinary X-ray photograph of wool or hair is a diffraction pattern arising from polypeptide chains which exist normally and even crystallise in some folded state out of which they may be pulled into a fully, or almost fully, extended state resembling that of the stable fibroin molecule.

The essential validity of this line of argument is demonstrated finally by the elucidation of the X-ray photograph of the keratin of feathers.8 The diffraction diagram given by the quill of feathers is a beautiful but complex fibre photograph which at first sight appears to be quite unrelated to that of either silk or mammalian hairs; but under its complexity it can be seen that it is really an elaboration of the type of photograph given by natural silk and stretched hair, apparently arising from a polypeptide pattern constructed from a linear sequence of at least eight amino-acid residues. The chains are normally in a slightly contracted state—by some 10 per cent.—but they may be pulled almost straight by the application of a strong stretching force. Before the feather fibres are ruptured the molecules are stretched by about 6 per cent. and then reveal a period along the chains which is only a little less than that found in silk and stretched hair. This period, which corresponds to the length of a single amino-acid residue (see above), is 3.5 Å for natural silk (fibroin), 3.4 Å for stretched hair (β-keratin), and 3.3 Å for stretched feather keratin.

## General Considerations on Protein Structure.

The X-ray photographs of silk and the stretched keratins are the only protein fibre photographs about which we may as yet feel any degree of

W. T. Astbury, J. Soc. Chem. Ind., 49, 441, 1930; J. Text. Sci., 4, 1, 1931;
 W. T. Astbury and A. Street, Phil. Trans. Roy. Soc., 230A, 75, 1931.
 W. T. Astbury and H. J. Woods, Nature, 126, 913, 1930; J. Text. Inst.,

<sup>23,</sup> T17, 1932.

7 S. A. Shorter, J. Text. Inst., 15, T207, 1924; J. Soc. Dyers and Colourists, 41, 212, 1925; J. B. Speakman, J. Text. Inst., 17, T457, 1926; 18, T431, 1927.

8 W. T. Astbury and T. C. Marwick, Nature, 130, 309, 1932.

confidence regarding even the main structural features, and we must confess ignorance as to any precise details of the individual chains. Poor as the photographs are when judged by the standards of ordinary crystal analysis, the fact that any photograph is obtained at all suggests that, at least in the more perfectly crystalline part of the fibre substance, the sequence of amino-acid residues cannot be extremely irregular. But it is clear that only a fraction of the fibre substance is in a sufficiently exact crystalline state to contribute to the fibre photograph proper, and it is an interesting and important point as to how far the X-ray indications apply to the fibre as a whole. The most reasonable point of view would appear to be that there is no such thing as a "pure" protein in the ordinary chemical sense,9 but that the X-ray photograph represents an ideal towards which the structure approximates, an ideal which may be thought of as the "true" structure of the given protein, which never actually occurs in an uncontaminated state, but which, so to speak, is sorted out by the process of X-ray diffraction because of its regularity. When we recall that even in one and the same wool fibre there are obvious variations in chemical composition, and that human hair, wool and animal hairs in general, porcupine quills, hedgehog spines, finger nails, horns, whale-bone, etc., all give rise to substantially the same X-ray photograph, it is difficult to avoid the conclusion that this photograph, in spite of the inconstant results of chemical analyses, does really correspond to a protein called keratin, which is the common molecular basis of all these epidermal growths and the structural theme from which all the numerous variations are developed. Similar remarks apply to natural silk, of course, and to collagen, muscle, etc., which also give rise each to a characteristic diffraction pattern. We are reminded at once of the structure of the silicates and the apparently complex chemical analyses which are a consequence of isomorphous replacement in and modifications of comparatively simple crystalline frameworks. Some such process must take place in the building-up of proteins, some process of amino-acid replacement which is not too serious to obliterate the identity or general properties of the compound, or make the X-ray photograph unrecognisable, yet sufficiently definite to act as a basis for the multitudinous protein variations which are actually met with. To reconcile the constancy of X-ray photograph with chemical variations we must postulate a kind of far-reaching isomorphism developed from origins which cannot be very complex in themselves. Whatever the purely chemical or physico-chemical difficulties involved in protein analysis, the message of X-rays seems to be that, deep down, there are underlying common features which hold out the greatest encouragement. If this idea is sound, these features should manifest themselves, directly or indirectly, in such photographs as are at present available, and even now should be susceptible of some sort of rough general treatment. With this end in view we may proceed to a brief discussion of some of the structural possibilities of the type of chain suggested above for natural silk and the keratins.

Taking the inter-bond angle for aliphatic carbon as the tetrahedral angle, 109° 28′, and the inter-bond angle for nitrogen as something of the same order, and perhaps rather less, 10 together with 1.54 Å as the

<sup>See, in this connection, S. P. L. Sørensen, C. R. des Trav. du Lab. Carlsberg, 18, No. 5, 1930. Also K. H. Meyer and H. Mark, Der Aufbau der hochpolymeren organischen Naturstoffe, p. 228.
L. Pauling, J. Amer. Chem. Soc., 53, 1367, 1931.</sup> 

interatomic distance between two carbon atoms (aliphatic) linked by a homopolar bond, and 1·3 Å as a mean estimate of the corresponding interatomic distance between carbon and nitrogen (in  $C_6H_{12}N_4$  it is 1·44 Å, in  $CO(NH_2)_2$  1·33 Å, in  $CS(NH_2)_2$  1·35 Å, and from spectral data 1·17 Å), we may write the general formula for a fully extended polypeptide chain as follows:—

CO CH NH CO CH NH CO CH NH CO CH NH 
$$R_3$$
  $R_5$   $R_5$   $R_5$   $R_5$   $R_6$   $R_7$   $R_8$   $R_8$   $R_8$   $R_8$   $R_8$   $R_8$   $R_9$   $R_9$ 

in which, as was first pointed out by Meyer and Mark, the length of a single amino-acid residue is probably about  $3\frac{1}{2}$  Å, the period found in the X-ray fibre photograph of natural silk.  $R_1$ ,  $R_2$ , etc., stand for various univalent side-chains, the discovery of the nature of which constitutes the chief problem when once, as in silk and the stretched keratins, the existence of the main chain is accepted. It will be noticed that the distance,  $3\frac{1}{2}$  Å, is only what may be called a "subsidiary period," because of the occurrence of a side-chain first on one side of the main chain and then on the other: a more definite "period," though still not necessarily the true unit of pattern of the chain, is twice this distance, 7 Å. This latter period is what is actually observed directly in the photographs of both silk and  $\beta$ -keratin, and indirectly in the photograph of feather keratin, though the last-named is sufficiently rich in X-ray reflections to show that the true period is at least eight times the length of a single amino-acid residue.

When protein chains such as the one depicted above cohere laterally to form crystalline, or pseudo-crystalline, bundles, the equilibrium form of the main chain will be determined principally by the nature of the side-chains. Both the main chain and the side-chains will possess considerable flexibility on account of free rotation about numerous bonds, and the final configuration of the multiple system will be the equilibrium compromise between all the various degrees of freedom. Meyer has given a valuable discussion of the cohesion and equilibrium of protein chains in general, 11 but we are concerned here more with the effects which may reasonably be looked for in X-ray photographs of combinations of chains. One of the simplest cases we can imagine is presented by the protein of natural silk, in which the side-chains, (-H) and (-CH<sub>3</sub>), are insufficiently active to interfere with a straightforward, and probably quite undistorted, cohesion of the main chains all along their length. The effective length of an amino-acid residue in fibroin is thus 3.5 A, the maximum yet observed, and there is no tendency under ordinary conditions for the main chain to be pulled into some shorter, crumpled, form. As one would expect, the lateral separation of the chain axes is of the order of  $4\frac{1}{2}$  Å 4 (not greater than 6·1 Å), 12 resembling that found in the hydrocarbons and their derivatives.

K. H. Meyer, Biochem. Z., 214, 253, 1929.
 O. Kratky, Z. physikal. Chem., 5B, 297, 1929; 11, 363, 1931.

But the case of silk fibroin, though extraordinarily illuminating, is rather exceptional on account of the insignificance and inactivity of its side-chains. Our great need at the moment is to clarify our ideas on the stability and lateral cohesion of the more general chain, decorated with active side-chains such as those of the glutamic and arginine residues. We have an instructive example, not too far removed from that of fibroin, in the structure of  $\beta$ -keratin, the stretched form of the protein of animal hairs. The chain configuration in  $\beta$ -keratin is not the stable configuration, for it collapses into a folded form (a-keratin) when the tension is released in the presence of water, that is, the stretched hair returns to its initial unstretched length. It is clear that there are certain side-chains which are sufficiently active to bring about this change, yet which are not powerful enough, either in their number, the nature of their electrical fields, or their state of linkage with neighbouring side-chains, to prevent an almost complete straightening of the main chain when tension is applied in the presence of water. The contractile or restricting influence of these side-chains cannot be completely eliminated by tension, however, since the effective length of the amino-acid residue in  $\beta$ -keratin is definitely shorter than that observed in silk. It is of the order of 3.4 Å,—probably rather less. From a study of the general physicochemical properties of animal hairs, we must conclude that the  $\beta$ -keratin chain can fold and recrystallise into a form of chain which is no more than half its maximum length. (The configuration and properties of this chain (a-keratin) have been discussed elsewhere 6 and will be gone into inconsiderable detail in a forthcoming publication.) The structure of feather keratin may be thought of as intermediate between the structure of hair keratin and that of silk fibroin. In the normal state, the interaction and cross-linkage of the side-chains fixes the main chain in a stable but contracted configuration in which each amino acid residue appears to occupy an average length of about 3.1 Å only. By the application of strong tension it can be partially pulled out of this configuration, as mentioned above, but the fibres break before complete straightening is attained.

The lateral dimensions of the generalised protein chain of the simple type shown above will probably be of two kinds, one, the smaller, analogous to the thickness of the fibroin chain and of the order of  $4\frac{1}{2}$  to 5 Å, and the other perhaps twice as great. The former is associated with the thickness of the backbone, and the latter with the space taken up by the side-chains. The latter alone occurs in the folded chain of α-keratin, but the former appears too, and very strongly, when the chain is pulled out into the  $\beta$ -form, suggesting a folding of the main chain in a plane transverse to the side-chain directions. Fig. I is a model of the most symmetrical form of the fully extended protein chain. plane of the atoms of the main chain (the direction of which is marked by arrows) lies perpendicular to the plane containing the side-chains when there is no distortion. Fig. 2 shows a model in which, through a certain amount of distortion of the main chain, the atoms of the latter have been constrained to lie approximately in the same plane as that containing the side-chain directions. It will be noticed that both forms are characterised by two principal lateral dimensions, the smaller of which must be something of the same order as the effective thickness of a longchain hydrocarbon or the fibroin chain.

The formation of well-defined groups of 2, 3, or 6 protein chains, in accordance with familiar crystallographic principles and by virtue

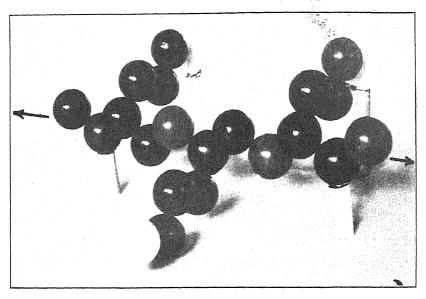


Fig. 1.—Symmetrical protein chain with main chain atoms lying in the plane perpendicular to the side-chains. The hydrogen atoms and the ketonic oxygen atoms have been omitted, the lighter atoms of the main chain being nitrogen. The side-chains shown are those of glutamic acid residues.

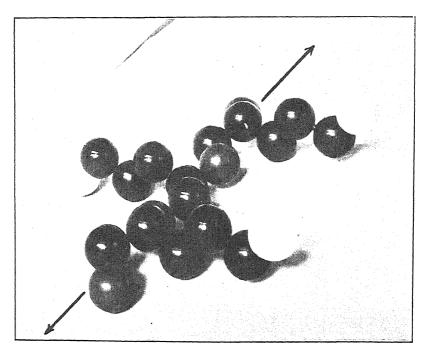


Fig. 2.—Slightly distorted protein chain with side-chain directions and main chain atoms all lying roughly in one plane.

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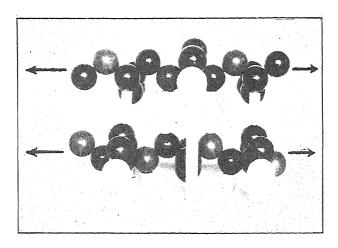


Fig. 4.—Model of the closest approach of symmetrical protein chains linked by attractions between C=O and N-H groups. The hydrogens and ketonic oxygens have been omitted.

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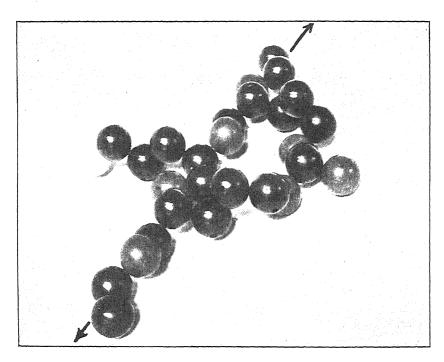


Fig. 5.—Internal peptide link between neighbouring side-chains of arginine and glutamic acid.

[See page 201.

of attractions between C=O and N-H groups, has been sug-

gested <sup>13</sup> as a possible explanation of Svedberg's results in his measurements by the ultra-centrifuge of the "particle weights" of proteins in solution. A similar suggestion with regard to the points of attraction has also more recently been put forward by Jordan Lloyd. <sup>14</sup> In view of the undoubted occurrence of a "side-spacing" of the order of  $4\frac{1}{2}$  to 5 Å in most of the X-ray photographs of proteins at present available, for example, silk,  $\beta$ -keratin, feather keratin, collagen, gelatine, the byssus threads of Pinna, the crystalline style of molluscs,\* the sclera and lens of the eye,\* certain cancerous tissues, etc., it would seem to be worth while to look a little more closely into this type of association to see whether it actually does involve a separation of the chain axes of the order observed. Omitting the side-chains, we may write two associated main chains as:—

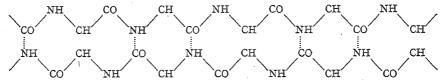


Fig. 3 shows the approach of two chains at the distance (4.65 Å) of the prominent side-spacing in  $\beta$ -keratin. Taking, from various crystallographic and spectral data, the average C—N distance to be 1.32 Å, the C=O distance to be 1.15 Å, and N—H distance to be 1.08 Å, we see that, even without allowing for the tilt of the N—H bond out of the plane of the main chain atoms, there remains a space of about 1.65 Å between the centres of the hydrogen and ketonic oxygen atoms, which seems to be reasonable enough in the light of our present knowledge of inter-atomic and inter-molecular distances. Fig. 4 shows a model of the most symmetrical arrangement of parallel protein chains linked on these principles. It will be seen that, with the side-chains alternately on one side and the other of the main chain, there is no interference with the closest possible approach of the main chain axes.

The question of the most probable value of the larger of the two side dimensions, that which we have associated with the lateral extension of the side-chains, is not so clear. From existing X-ray photographs it appears to lie generally somewhere between 9 and 10 Å. Whether this is an average value arising out of the flexibility of the side-chains, or whether it is imposed by one or more particular types of cross-linkage, it is not yet possible to say with any certainty. If we accept, however, its existence as an experimental fact, it is possible to make an estimate of the density of dehydrated protein which is in very satisfactory agreement with observation. The average molecular weight of the aminoacid residues known to occur in proteins is about 120. Thus, if D is the average density of a structure built according to the principles outlined above, we have

9.5 
$$\times$$
 4.5  $\times$  3.5  $\times$   $D \approx$  120  $\times$  1.65, whence  $D \approx$  1.3.

W. T. Astbury and H. J. Woods, Nature, 127, 663, 1931.
 D. Jordan Lloyd, J. Soc. Chem. Ind., 51, T141, 1932.

<sup>\*</sup> For the use of these photographs I am indebted to Miss T. C. Marwick.

In view of the definite individuality of the various existing protein photographs—for instance, though the X-ray photograph of the sartorius muscle of the frog is remarkably like that of unstretched wool and hair ( $\alpha$ -keratin), there are nevertheless unmistakable differences—and having regard to what has been said above on the question of the "true" structure of any given protein, it seems advisable to keep well in mind not merely the possibility but the probability of fundamental structural

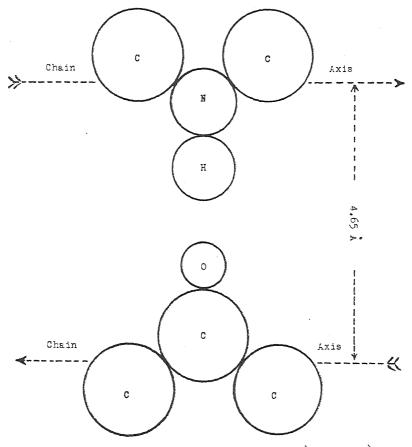


Fig. 3.—Diagrammatic representation of the approach of C=O and N—H groups in neighbouring protein chains. C—C = 1.54 Å, C—N = 1.32 Å, C=O = 1.15 Å, and N—H = 1.08 Å.

regularities when considering the significance of the spacing just associated with the lateral extension of the side-chains. It must be repeated that, unsatisfactory as are protein photographs from the point of view of the strict geometrical theory that has proved so prolific in the study of compounds of low molecular weight, each has certain well-defined periodicities and other distinctive features of its own which point to the existence of specific stereochemical groupings of no arbitrary type. It is impossible to contemplate the beautiful fibre photograph of feather keratin without

arriving at the strong conviction that it must arise from a definite sequence of amino-acid residues linked always in substantially the same fashion. Furthermore, it is not necessary to suppose that the protein "molecule" is based always on a single polypeptide chain, straight. crumpled, or folded: cross-linkages of a familiar chemical nature, though probably not in great variety, are not unlikely, for example, the cystine and internal anyhydride linkages, 15 the internal salt linkage, 16 and the lateral peptide linkage.8 Internal peptide linkages between side-chains of one and the same main chain are also not impossible, for, as Meyer has shown,11 we may always expect a shortening of the main chain at the neutral point on account of attraction between free -NH2 and free -COOH groups and the formation of "zwitterions." Fig. 5 is a model of the following internal peptide link between neighbouring arginine and glutamic acid side-chains:-

It will be noticed that it involves a certain degree of distortion, and therefore of contraction, of the main chain such as is revealed by X-ray examination in various fibrous proteins.

It should be realised that the above suggestions are all of a tentative nature, put forward in the effort to explain the observed X-ray regularities. One clear point emerges, however, and that is that any distortion of the main chain due to interaction of the side-chains, whether of the same or neighbouring main chains, must lead to contraction. We can see now why only in silk fibroin is found the theoretical maximum length (3.5 Å) for an amino-acid residue: even under tension the keratin chain is slightly shorter, while in other fibrous proteins, such as collagen, the change is so pronounced that difficulties of interpretation arise immediately. The case of collagen and gelatine, which give rise to a common X-ray photograph which has been investigated by a number of workers, 17 is particularly intriguing. The most obvious "subsidiary period" along the polypeptide chain has a length of about 2.8 Å, but Susich's measurements 11 indicate that a more exact repetition of pattern occurs also at a distance of about 8.4 Å. Meyer 11 has suggested that this latter distance, 8.4 Å, corresponds to the period, 7 Å, observed in silk fibroin, that is, to the length of two amino-acid residues; but it seems

<sup>&</sup>lt;sup>15</sup> W. T. Astbury and H. J. Woods, J. Text. Inst., 23, T17, 1932.
<sup>16</sup> J. B. Speakman and M. C. Hirst, Nature, 128, 1073, 1931.
<sup>17</sup> P. Scherrer, Zsigmondy's Lehrbuch der Kolloidchemie, III, 1920, p. 408;
R. O. Herzog and H. W. Gonell, Ber., 58, 2228, 1925;
R. O. Herzog and W. Jancke, Ber., 59, 2487, 1926, and 53, 2162, 1920;
J. R. Katz and O. Gerngross, Naturw., 13, 900, 1925;
O. Gerngross and J. R. Katz, Koll. Z., 39, 181, 1926;
G. v. Susich in K. H. Meyer, Biochem. Z., 214, 265, 1929;
J. J. Trillat, C.R., 190, 265, 1930;
O. Gerngross, O. Triangi and P. Koeppe, Ber., 63, 1603, 1930;
K. Herrmann, O. Gerngross and W. Abitz, Z. physikal. Chem., 10B, 371, 1930.

more reasonable, in view of the considerations set out above, to conclude that it is really the length of three residues—perhaps glycine, proline, and oxy-proline—each occupying on an average 2.8 Å. If the residues follow one another in collagen and gelatine in what we may call the normal sequence of the generalised protein chain, it is difficult to see how each could take up 4.2 Å; but if, on the other hand, the sequence occurs in sets of three, we may feel sure from the above reasoning that a contraction must take place, because in the symmetrical chain the side-chains occur alternately on one side and the other of the main chain. We can group the side-chains in all sorts of ways by twisting the main chain about its axis, but this involves a distortion from the symmetrical form (Fig. 1), and a distortion always gives rise to a shortening of the average length associated with each residue, even without taking into consideration the probable interaction of the side-chains. When the latter, too, is allowed for, we see that the most satisfactory picture of the collagen or gelatine chain that can be built up from the results of X-ray analysis is that of a polypeptide twisted about its main axis so that the side-chain pattern is made to occur, not in sets of two, but in sets of three: to the distortion consequent on this operation must be added that due to some linkage or strong interaction of the side-chains this supposition and that of the twisting into sets of three residues are, of course, one and the same thing; if one is true, the other followswith the result that the theoretical maximum subsidiary period is reduced from 3.5 Å to 2.8 Å, and the period 7 Å is raised to 8.4 Å. Additional support is lent to this view by the observed values of the side-spacings of the X-ray photograph; as we should expect from a crumpling of the main chain, these are rather greater than the "normal" values we have postulated above. Instead of about 4½ Å and 9½ Å we find two spacings, one of which is over 5 Å and the other about II Å.

We may suitably conclude this section by a few remarks on the subject of long-range elasticity in protein fibres. As already mentioned, this has been submitted to a valuable discussion by Meyer 11, 1 on the basis of the mutual attractions between free -NH<sub>2</sub> groups and free -COOH groups belonging to side-chains of the same main chain. More recently the work of Bernal 18 on the crystal structure of the aminoacids has shown how such considerations control the configuration of these acids also in the solid state. It seems clear that this theory would satisfactorily explain at least the more obvious features of the long-range elasticity of animal hairs and the reversible transformation between the folded  $\alpha$ -keratin chain and the fully extended  $\beta$ -keratin chain. It has already been pointed out above that only in the extended  $\beta$ -form do we observe the shorter side-spacing which we have associated with the thickness of the backbone, but the long side-spacing is common to both forms. Thus if, as we have postulated, the long spacing corresponds simply to the lateral extension of the side-chains, a folding of the main chain in a plane transverse to these, brought about directly by their tendency to approach in the presence of water as closely as possible to one another, would give an adequate broad interpretation of the elastic properties of hair in terms of the actual X-ray data. This is only the briefest possible outline of the problem, of course; there are numerous interesting points regarding the form and properties of the keratin chain which will be discussed in detail elsewhere.

<sup>&</sup>lt;sup>18</sup> J. D. Bernal, Z. Krist., 78, 363, 1931; J. Hengstenberg and F. V. Lenel, Z. Krist., 77, 424, 1931.

We shall leave this section on a final note of interrogation. Why are the X-ray photographs of α-keratin and muscle 19 so remarkably alike? The fact that the a-keratin chain is sufficiently regular to give rise to a definite fibre photograph even after a large number of extensions and relaxations suggests that it is one expression, at least, of some welldefined way in which the protein chain may be stabilised in a strongly folded form. If, as seems plausible, the muscle chain is also constructed according to this or a closely similar pattern—we are not speaking here so much of the nature of the side-chains as the form of the backbonewhy can it not be transformed by tension into a fully extended state analogous to that of  $\beta$ -keratin? Experiments to test this point have been carried out by the writer in co-operation with Mrs. S. Dickinson of the Physiology Department of Leeds University, but no transformation has as yet been observed. One explanation, based on the fact that the spacings of the muscle photograph are slightly smaller than those of the a-keratin photograph, is suggested at once by the X-ray data. It is that either there is a closed chemical bond which effectively "bolts" the muscle chain, so to speak, or else the number of active side-chains is so great that their mutual attractions cannot be overcome by simple tension without rupturing the structure as a whole. The apparent paradox that the X-ray photograph of stretched muscle is analogous to that of unstretched hair has already been resolved by experiments which have received a preliminary mention in a recent publication by H. J. Woods and the present writer. Unstretched hair is not in a state of maximum contraction, but may still be contracted under suitable conditions to about half its original length.

## The Nature of the Micelle.

The swelling of wool has been investigated in considerable detail by Speakman.<sup>20</sup> From arguments which need not be reproduced here he concludes that wool is undoubtedly built up of micelles, in the sense of submicroscopic particles which to all intents and purposes are not penetrated by water and similar swelling agents, and that these micelles cannot be more than about 200 Å thick. This, of course, agrees with the optical properties \* and the main conclusions of X-ray analysis; but, as we feel now, it really only touches on the fringe of the problem. There are so many interesting points of biological importance involved in the question of the true nature of the micelle, that it may serve a useful purpose to indicate briefly certain other considerations which appear to have a bearing on the matter.

In the first place, animal hairs do not appear to show any internal slipping when they are stretched: not only can they be made to recover their original length,7 but also, on certain treatment after which the term "unstretched length" loses its significance and, in fact, becomes meaningless, they can be made to assume a state of surprising contraction.6 The whole fibre behaves effectively as a continuous extensible spring. Neither from the elastic properties, nor from attempts to dissolve wool and re-precipitate it unchanged, nor, in actual fact, from any property at present known, do we find any indication of sharp discon-

<sup>19</sup> See, for example, G. Boehm and K. F. Schotzky, Naturw., 18, 282, 1930.

<sup>&</sup>lt;sup>20</sup> J. B. Speakman, *Proc. Roy. Soc.*, **132A**, 167, 1931.

\* The optical properties of the keratins, in the light of the more recent structure. tural knowledge, are now being examined in detail by R. J. Barnes and the author.

tinuities of molecular or crystalline structure. It is as though we ought to think of this structure simply as a mass of roughly parallel protein chains which have crystallised out as best they can. It has already been shown 6 how some such concept is necessary to explain the phenomena of "Nachwirkung" in natural fibres, and there is nothing fundamental in the swelling or X-ray results to belie it. However, the suggestion which we specially wish to put forward here is that of the analogy between the micellar structure of fibres and the "secondary structure" postulated recently by Zwicky 21 to explain certain general features of crystal architecture which appear to be essential for its stability. In this author's own words, "one of the most conspicuous phenomena very often exhibited by the solid state is a peculiar co-existence of perfection and imperfection in crystals. . . . From the conception of a secondary structure, however, . . . the co-existence of perfection and imperfection in crystals may be accounted for." It is thus perhaps not unreasonable to consider whether the micellar structure of fibres, which is characterised so clearly by a mixture of perfection and imperfection of the crystalline state, may not really be the counterpart in compounds of high molecular weight of the well-known mosaic or secondary structure of more familiar crystals, which, among other effects, can result in a mechanical strength hundreds or thousands of times smaller than what would be expected from ideal lattice theory. In the case of the non-elastic fibres, cellulose and silk, which extend by internal slipping. 1, 6 the X-ray photograph is substantially unchanged on stretching the fibre, while even after solution and reprecipitation we again obtain the same unmistakable indications of the existence of the crystalline aggregates which have been identified with Nägeli's micelles; but still there is no evidence for the pre-existence of sharply defined micelles. The arguments for their pre-existence rest on acts of disruption and are therefore open to suspicion: rather does the available evidence point to a self-contained system riddled through and through by crystallisation "faults."

In this connection we may recall the experiments of Goetz on the thermal expansion of bismuth crystals.<sup>22</sup> These experiments bring out clearly the considerable discrepancy which exists between the coefficient of expansion as determined on the macroscopic crystals and the coefficient as determined by X-ray measurements of the lattice spacings. Similarly, there is an even greater discrepancy between the percentage swelling of a wet hair fibre as observed on the visible fibre and the percentage swelling as derived from the results of X-ray analysis. Experiments by F. Happey and the author, which will be described in detail elsewhere, have shown that it is not strictly true to say that the adsorbed water does not penetrate into the interior of the micelles, but that actually the first part of this water—that is, starting from complete dryness-does penetrate between the protein chains to cause a lateral swelling of the order of a few per cent., chiefly by an increase of the longer spacing which we have associated above with the lateral extension of the side-chains. Furthermore, other swelling agents also give rise to similar spacing changes, while some, at sufficient concentration, interpenetrate the crystalline structure so strongly as to destroy the X-ray photograph altogether. The logical outcome of such observations as these is the conclusion that the term "micelle size," as used in discussions

<sup>&</sup>lt;sup>21</sup> F. Zwicky, Proc. Nat. Acad. Sci., 15, 816, 1929; 17, 524, 1931; Physical Rev., 38, 1772, 1931; 40, 63, 1932.
<sup>22</sup> A. Goetz, Physic. Rev., 40, 643, 1932.

of swelling phenomena—and indeed, as we have suggested above, even in its most general acceptance—has no precise meaning, but rather is a function of both the swelling agent and previous swelling history. With an "inactive" liquid such as benzene the "micelle size" is limited only by the grosser imperfections of structure, while in the case of swelling by aqueous alkalis the micelle may be synonymous with even a single molecular chain.

As the swelling agent penetrates more and more between the elementary chains, both the X-ray "fibre photograph" and the birefringence gradually disappear: the former is the first to be eliminated, as one might expect. By combining such effects with a knowledge of the chain thickness, it is possible to make a rough estimate of the average thickness of the crystalline, or pseudo-crystalline, bundles of chains which are relatively impervious to water. In view of what has been said above, the underlying assumptions are perhaps rather crude, but they lead to results of undoubtedly the right order.

Let D be the effective thickness (the separation distance) of a molecular chain in the dry fibre, and suppose there are n chains in the thickness of a bundle and m bundles in the thickness of a fibre. Further, let the thickness of the fibre when dry be  $T_o$ , when wet with water,  $T_w$ , and when swollen by some intra-crystalline swelling agent,  $T_s$ . Then

$$mnD = T_o, \qquad . \qquad . \qquad . \qquad . \qquad .$$

and if  $D_w$  is the separation distance of the nearest chains of neighbouring bundles when the fibre is swollen with water,

$$m(D_w - D) = (T_w - T_o).$$
 (2)

Now let us assume that when the X-ray photograph and the birefringence are destroyed, all the individual chains are separated by the same distance,  $D_w$ , as separated the bundles in the water-swollen state. Then

$$mnD_w = D_w T_o/D = T_s. . . (3)$$

Whence the thickness per bundle (nD) is equal to :—

$$D(T_s - T_o)/(T_w - T_o).$$

If  $T_o$  is taken as 100, then  $(T_w-T_o)$  is approximately equal to 18 for Cotswold wool. The X-ray photograph of the same fibre is destroyed when the latter is swollen in a 3 per cent. aqueous solution of caustic soda. The linear increase in fibre diameter is then of the order of 170 per cent., that is,  $(T_{\hat{s}}-T_o)$  is roughly equal to 170. Thus it follows from the above relation that there must, on the average, be something like ten chains in the thickness of each of the crystalline bundles which are relatively impervious to water. Finally, from the general considerations on protein structure set out in the preceding section from which the opinion was formed that the longer side-spacing (9.8 Å for Cotswold wool) represents the thickness of the protein chain in the direction of the side-chains, and from the experiment mentioned above which indicates that it is chiefly the side-chain dimension of the main chain which is affected by water adsorption, we may conclude that the average thickness of the main-chain bundles which are relatively impervious to water is no more than about 100 Å, and possibly less.

<sup>&</sup>lt;sup>23</sup> J. B. Speakman, J. Soc. Chem. Ind., 49, T209, 1930.

# GENERAL DISCUSSION.

Mr. W. T. Astbury (Leeds), in introducing his paper for discussion, added: We have just recently made some observations which appear to throw a very considerable light on the problem of variability in protein structure—why the X-ray diagram is preserved in spite of obvious differences in chemical composition. It was apparent from the beginning that the sequence of eight amino-acid residues (24.8 Å) in feather keratin was only an approximation to the true pattern, and that the latter would in all probability turn out on closer investigation to be very much longer; and now Miss Marwick has obtained a very beautiful photograph in which the "spot" corresponding to the spacing 24.8 Å is resolved into two very close spots which appear to be 12th and 14th orders. The true pattern in the protein chain of feather keratin thus repeats at a distance of about 309 Å, that is, the length of a hundred amino-acid residues! It is now clear that there is much greater latitude for structural replacement without destroying the essentials of the X-ray photograph than appeared possible with the small patterns of silk and hair. These are obviously only pseudopatterns—patterns within patterns, so to speak—in some gigantic sequence analogous to that of feather keratin.

In conclusion, I wish to express my indebtedness to the Worshipful Company of Clothworkers and the Government Grant Committee of the Royal Society for the funds which have made these researches

possible.

**Dr. D. Jordan Lloyd** (London) said: Mr. Astbury in his very interesting paper has assigned to silk the title of the "ideal" protein, since the long backbones of its molecules lie in a fully extended condition and show a conspicuous absence of polar groups. He has suggested that the introduction of polar groups into the protein molecule will always lead to a tendency to contract, with the production of a more or less spiral structure, contraction being particularly marked in those proteins in which the basic and acidic groups are in balance since there will be no forces of repulsion to keep the backbone extended. Regarding the matter from a biological standpoint, the most striking feature of proteins as a class is their intimate connection with cell life and biochemical activity. It might be anticipated, therefore, that the molecular structure of any particular protein would show some connection with its biological function, and further that an open or straight chain structure of the protein backbone would occur in tissues, showing great metabolic activity and a more or less closed or spiral structure in tissues which were biochemically inert. The few facts available are interestingsilk is a secretion of the body and is metabolically absolutely inert, yet it has the extended molecular backbone: this, however, can be accounted for by the absence of polar groups. The X-ray pattern of wool and muscle suggested similar contracted chains in both these fibres. Wool fibres are certainly free from any biological activity, but muscle fibres are intimately connected with one of the most characteristic forms of activity. At first sight, this appears paradoxical but further consideration shows that muscle fibres themselves appear to be remarkably stable structures, existing in close connection with chemical reactions involving the breakdown of a carbohydrate with the release of energy. The muscle proteins are not involved in any way in the cycle of chemical change which occurs, and indeed they can be likened to the mechanical

parts of an internal combustion engine. A group of proteins which undoubtedly is involved in the chemistry of cell activity is found in the protamines which occur as salts of nucleic acid in the spermatozoa of fish (and presumably other animals) and which are intimately connected with nuclear division and cell growth. The molecules of the protamines are heavily loaded with polar groups, nearly all of a basic character and the electrical repulsions between these might be expected to keep the backbone of the molecule extended. If this occurs, it would follow that the form of the molecule would lead to the highest potentialities for chemical activity since all the guanidine groups in the side chains would be freely available to molecules of water or other substances. Experimental evidence on this point will be eagerly awaited.

Professor H. Mark (Wien) said: From the very interesting results of Dr. Astbury's investigations it is quite clear that cross linkages play an important rôle in the chemical behaviour of proteins. During the discussion regarding the field of cellulose nothing was said about such linkages, but it seems to me that they also are of some importance in cellulose chemistry. It has often been pointed out that the native state of cellulose has something particular in respect to the swelling and solution properties. Very slight treatment of native fibres changes their behaviour much more than the identical treatment when it is applied at a later stage to the same sample. This effect is not easily to be understood from a pure main valence chain model. It might be possible that a small number of cross linkages between the parallel chains are responsible for the special behaviour of the native state. This could be compared with the difference between a slightly vulcanised rubber and a natural one, a point to which K. H. Meyer first drew attention.

Professor R. A. Peters (Oxford) said: As a biochemist, I do not know how far there is any alternative explanation of the facts upon which Dr. Astbury has built the view of straight protein chains. Owing to its great biological interest, it can hardly be too severely tested, and must become of moment for cell biochemistry if applicable to the soluble proteins, though the data of Svedberg and his colleagues rather indicate that ovalbumin and many other proteins have spherical molecules. Many will recall the discussion at the previous colloid meeting of the Society. Some of us who are face to face with the diverse activities of the living cell (for I am sure that I do not stand alone), feel the need for postulating some organised protein structure, responsible in the last limit for co-ordinate activity. This could hardly be constructed without a backbone of chains, and any certainty reached upon their existence would give us much more confidence in feeling our way.

Dr. J. R. Katz (Amsterdam) said: Mr. Astbury's interesting results about the change in the X-ray pattern of wool fibres through stretching is probably somewhat similar to the changes in the X-ray pattern of rubber through stretching, which I have published in 1925. In the unstretched state rubber shows an amorphous ring, while stretched it has a fibre diagram (with a weakened amorphous ring). Through

<sup>&</sup>lt;sup>1</sup> Naturwiss., 13, 411, 1925; Gummi-Zeitung, 1927, Heft 36 and 37; and Ergebn. exakt. Naturw., 4, 171-185, 1925, contain together most of the facts I had found in 1925-27. For the X-ray pattern of synthetic rubbers and their change in stretching, see Koll. Beih. (Ambronn-Festschrift), p. 344, 1926 and especially Chemiker-Zeitung, 51, 53, 1927. For photometric studies of this phenomenon see E. A. Hauser and H. Mark, Koll. Beih., 22, 463, 1926; 25, 64, 1926

the stretching a part of the "amorphous" substance has become "crystalline"; the more so the stronger the stretching. All these minute little crystals are lying with one axis parallel to the direction of stretching, giving a typical fibre diagram.

In the case of rubber it has up to the present remained uncertain whether a really important change in the form of the molecules occurs. If the molecules are spirals in the unstretched state, getting the form of straight lines in the particles which have become "crystalline," then the stretching of rubber must be an extremely complicated phenomenon. How do all these molecules revert to their exact former positions, after each of them has curled up again into a spiral? I do not think this mechanism of the phenomenon very probable, although I must admit that I do not understand the mechanism whereby it is possible to stretch rubber to the tenfold length.

I have tried to approach this problem by analysing the amorphous ring of unstretched rubber and comparing it with the X-ray diagrams of liquids. It is with this purpose that I studied the X-ray diagrams of liquids extensively in 1925-1928. When beginning these researches, in 1925, I had the conception that the parallel arrangement of the molecules which becomes manifest in stretched rubber must already be preformed in unstretched rubber. I supposed that the arrangement of the molecules in "amorphous" rubber is much of the same kind as in nematic substances: long molecules lying parallel, but not being ordered regularly in the transverse dimensions. Already in 1925 I discussed the long chain form of the rubber molecule. Through stretching, this higher degree of order is formed, the X-ray pattern of a crystalline substance appears, but with a discontinuity: rubber only shows a crystalline pattern after a stretching of 75 per cent.

The comparison of the X-ray pattern of amorphous rubber with that of different liquids seemed to show that the period of identity of the amorphous ring of rubber and of liquid hydrocarbons measures the transverse distance of hydrocarbon chains lying parallel in small groups. This distance is a little larger than in normal hydrocarbons due to the fact that the rubber (isoprene) chain carries methyl groups. It was in this way that I was brought to seek for a group structure in liquids and found it about the same time as Professor Stewart (Iowa City) and the collaborators of Professor Raman (Calcutta).

If this conception is right, the axes of the groups of long chained rubber molecules must be parallelised during stretching before they change into a crystalline arrangement. In unstretched rubber the longer axes of these groups lie distributed at random. In the beginning of the stretching these groups must be parallelised (like the groups of molecules in the nematic state in a magnetic field). I therefore thought it an important fact that Bjerkén had found a different value for the optical anisotropy of rubber in proportion to the stretching at low and at high degrees of stretching. At low degrees we are measuring the effect of the parallelisation of the molecules or of the nematic "groups," at stronger stretchings there would be found the effect of the parallel crystals. At my suggestion Mr. van Geel and Miss Eymers undertook to measure again

<sup>&</sup>lt;sup>2</sup> Fikentscher and Mark.

<sup>&</sup>lt;sup>3</sup> For the analogy of unstretched rubber with nematic substances see *Ergebn. exakt. Naturw.*, 4, 171-185, 1925.

<sup>4</sup> Literature in Z. angew. Chem., p. 329, 1928.

<sup>\*</sup> Literature in Z. angew. Chem., p. 329, 1925. 5 Koll. Z., 37, 22, paragraph 5, 1925.

the optical anisotropy of rubber in Professor Ornstein's laboratory. They found below 75 per cent. of stretching a curve closely resembling the curve for the anisotropy of nematic substances in a magnetic field; at about 75 per cent. there is a clear discontinuity in this curve.<sup>6</sup>

I have quoted these facts at length, because they all seemed to show that in the stretching of rubber the form of the molecules may not change very materially. The results of Dr. Astbury with wool, on the contrary, seem to indicate a clear change in the form of the molecules. So they may give support to the view that in the stretching of rubber, too, the form of the molecules is strongly changed. But in the case of rubber we do not yet see clear. Perhaps the determination of the heat developed in the stretching of wool fibres may throw some light on this question. After Joule first found it for rubber, all rubber-like substances have proved to develop heat when stretched. If the heat of swelling of stretched and unstretched wool fibres is determined in a strong swelling agent which causes the permanent stretching to go back, it may be possible to determine the heat of stretching in wool fibres (cf. an

analogous experiment of Hock with rubber).

Mr. Astbury, in reply, said: I should first like to say how very much I appreciate the point of view of Professor Peters and others who, like him, are anxious to acquire a clear mental picture of protein structure, yet are puzzled by certain physico-chemical features which as yet do not appear to harmonise with such a picture. But it is the aim of structural crystallography, as developed by X-ray methods, to supply a true stereo-chemical scheme of the solid state, and its successes over the last twenty years have been so striking—often, as in the case of the silicates and many other inorganic compounds, when classical chemical methods had failed to arrive at any satisfactory conclusion—that we cannot now but regard it as affording some of the most convincing arguments in modern research. I think that very few people are inclined to question its very great contributions to the solution of the problem of the structure of cellulose and its derivatives, yet it is along essentially similar lines of attack that the proteins are now being approached: and already the results explain so much (especially in the case of the keratins, as will be seen when the complete data are set out in a forthcoming publication) that I feel we should find overwhelming difficulties in interpreting them otherwise-difficulties many times more serious than those associated with the values of certain physico-chemical constants at present accepted. If I may, I should once more like to refer Professor Peters to my comments on the papers by Drs. Jordan Lloyd and Phillips, Drs. Speakman and Hirst, and Mr. Hughes, in particular the last-mentioned. Is it not very significant that from purely crystallographic data one can arrive at the results of Hughes and Gorter and Grendel, and, as I strongly believe 7 even those of Svedberg?

As Dr. Jordan Lloyd has also pointed out in her valuable paper with Dr. Phillips, the influence of organised structure on the properties of proteins can be very great indeed. More than anything else, I think we ought to allow for loss of mobility, and the restricted range of action of the various radicles involved. From my own experience, perhaps the simplest example I can quote is that of stretched wool or hair. It

W. C. van Geel and J. G. Eymers, Z. physik. Chem., 3B, 240, 1929.
 See W. T. Astbury and H. J. Woods, Nature, 127, 663, 1931.

is obvious that the physical properties of stretched hair are different from those of unstretched hair, yet it is equally true that the chemical properties are quite different. For instance, stretched hair reacts almost immediately with steam, as is shown at once by the loss of elasticity and by clear changes in the X-ray photograph. Another point that has recently occurred to me, by way of a conversation with Dr. Speakman in which he pointed out to me that sulphuric acid in the swelling of wool appears to simulate the properties of a mono-basic acid, is that in reactions with such a chain- or ladder-structure as must be postulated to explain the X-ray effects and the general physical and chemical properties of wool, we might expect all acids to behave in a way as mono-basic acids, because of the distance of separation of the basic side-chains in their distribution along the main-chains. In the case of wool, Speakman has shown this distance to be on the average equivalent to the length of ten residues (see also my comments on Speakman's paper, where the same result is used to explain quantitatively the "super-contraction" of wool and hair).

X-ray analysis does not lead exclusively to the concept of the straight chain in protein structure: on the contrary, as I have tried to bring out in my paper, it leads in general to the concept of the crumpled or even folded chain, from which it is not a long step to explain the main features of the phenomena of denaturation.8 It is true that arginine might be inserted backwards, so to speak, into the protein backbone, so as to leave the α-amino-group in the side-chain, and such a change would not be immediately detected by X-ray methods on account of the fact that the guanidine group would then occupy a length practically equal to that of a residue with its a-amino-group incorporated by peptide linkage in the main-chain, yet this is the only possible case of such an alternative: we are still left with the fundamental finding of X-ray analysis, that the protein system as a whole is a chain structure, the dimensions of which correspond to simple peptide linkage by way of α-amino-groups. I think that there is no escape from this conclusion for all the other amino-acids; and even if we decide to except arginine, then I have no doubt that Dr. Speakman and Professor Elöd can bring forward arguments against such a procedure in the case of keratin, at the very least.

To my mind the conclusions of X-ray analysis on protein structure will ultimately prove of immense value in the study of the activities of the living cell. Already in the method of parallel alignment mentioned we can see glimmerings of the process of auto-catalysis by which a protein, in successive generations, builds up a replica of itself without the intervention of mirror-image forms. Perhaps, too, we have here the basis of the "gene" and the origin of mutations. In any case I feel that we have now laid some strong foundations on which to build, and surely many of our present difficulties will soon disappear.

Mr. W. T. Astbury in reply (communicated): I am much indebted to Dr. Katz for his remarks on the problem of rubber in relation to that of wool and hair. I do not think, however, that there can be any doubt in either case that extension proceeds by unfolding of long molecular chains, for above all we have to remember that these two substances, rubber and keratin, are distinguished by long-range reversible elastic properties. (In the case of wool and hair the reversibility is perfect,

<sup>8</sup> See, for example, C. Rimington, Nature, 127, 440, 1931.

both with regard to the form of the fibre and the X-ray photograph.) There does not seem to me to be any need to assume that each rubber chain returns exactly to its original form; if the amorphous state were merely statistically the same, it would be sufficient to explain the X-ray results at least. But a more powerful argument still is afforded by the range of the extension, a matter of 900 per cent. I have gone into this question more fully in my comments on the paper by Mr. J. M. Preston on the refractive indices of fibres, and it seems clear that the mere alignment of a perfectly random distribution of long chains or bundles will by no means yield the observed extension. One hundred per cent. seems to be the absolute maximum by such a process, whereas the mechanism of molecular unfolding offers possibilities of a much higher order. Besides, as I have just said, the extension of rubber is reversible. and there does not appear to be any particular reason why the process of parallelisation of long thin bodies should be anything more than partially reversible. Indeed, in the case of natural silk and cellulose fibres, we know definitely that it is not. A full discussion of the problem of the elasticity of wool and hair will be published shortly, when it will be shown conclusively, I think, that it is all a question of molecular unfolding. At the moment, too, I cannot see any escape from a similar conclusion to explain the main elastic properties of rubber.

# THE ELECTRICAL AND MECHANICAL PRO-PERTIES OF PROTEIN FILMS.

By A. H. Hughes.

Department of Colloid Science, Cambridge.

Received 8th August, 1932.

In view of the fact that many naturally occurring fibres have been shown to contain oriented protein molecules, it seemed advisable to examine in detail the unique properties of a phase interface as a source of molecular orientation, with reference to surface films of individual proteins.

It is well known that films of various types of proteins are readily formed at the surface of aqueous solutions and such films have been examined by many workers, notably by Gorter and Grendel, and by du Noüy, who has stressed the biological importance of the formation of these films.

In order to obtain precise quantitative data on the properties of these films it is essential to ensure that the films are uniform and reproducible. There are two methods of obtaining protein films: first by accumulation at the surface of a protein sol; secondly, by spreading the protein directly on the water surface.

Du Nouy has examined in detail the fall in surface tension with time accompanying the former process, and deduced a value of the order of 30-40 Å.U. for the thickness of the resulting film. Gorter and Grendel,

Gorter and Grendel, Proc. Kon. Akad. Amst., 29, 371, 1926.
 Du Noüy: "Surface Equilibria of Biological and Organic Colloids," 1926.

on the other hand, spread the protein from a small volume of an aqueous solution blown horizontally on to the surface and followed the force-area characteristics of the film by means of a Langmuir-Adam trough.

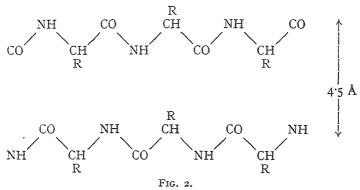
From the maximum spreading areas a minimum film thickness of about 7 Å.U. was obtained.

In either of these two methods the numerical results are open to doubt, since the film obtained from a colloidal solution of the protein is likely to be composite and far from homogeneous, except after waiting for a considerable time for the complete spreading of the colloidal micelles.

Although no very clear picture of the constitution of these films was obtained, the interesting observation was made by Gorter and Grendel<sup>3</sup> that the maximum spreading areas of different proteins on water was about the same, namely 1.0 10 - 7 gm./sq. cm. whether the proteins had molecular weights, as determined by Svedberg, of 34,500 or two, three, and six times this value. This indicates the presence of some structure common to films of all these proteins, irrespective of their class

The recent work of Astbury <sup>4</sup> and of Meyer and Mark <sup>5</sup> on the X-ray structure of natural proteins provides ample evidence in support of the peptide chain theory of protein structure. It would thus appear that a true "unimolecular" layer of a protein should possess the same general properties independent of molecular weight, which becomes of secondary importance in the structure of the films.

In a recent paper <sup>6</sup> a new method of obtaining protein films has been described, by which the film is spread from a minute particle of the solid protein placed on the liquid surface. The weight of protein in the film is measured on a simple micro-balance, and the films are examined quantitatively by the methods of surface pressures and of surface potentials. It was shown that for gliadin homogeneous films can be obtained



with a mean thickness as low as 3 Å.U. Compression of the film is accompanied by a change from a fluid film to a gelatinous type of film under a compression of about 15 dynes per cm. The vertical component of the electric moment of the film, obtained from the values of the surface potential, decreases markedly in the transition to the gelatinous film.

In the light of the X-ray data for proteins and amino-acids it is possible to assign a general structure to the protein film in its various stages of compression, on the supposition that the basic polypeptide chains of the protein are stretched out flat on the surface of the liquid in the most expanded state of the film (Fig. 1). On compression, the side chains to the main polypeptide chain are forced out of the surface, the main chains being now in close proximity, with a spacing of about 4.5 Å.U. in the gelatinous film (Fig. 2).

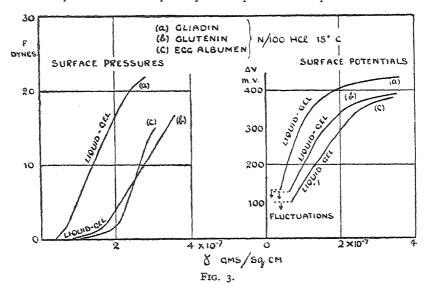
The surface properties of some other proteins have now been examined.

<sup>&</sup>lt;sup>3</sup> Gorter and Grendel, Proc. Kon. Akad. Amst., 32, 770, 1929.

<sup>&</sup>lt;sup>4</sup> Astbury, Phil. Trans. Roy. Soc. 230A, 75, 1931.
<sup>5</sup> Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Leipzig, 1930.
<sup>6</sup> Hughes and Rideal, Proc. Roy. Soc., 137A, 62, 1932.

#### Egg Albumen and Glutenin.

The results obtained with egg albumen, glutenin and with gliadin are shown in Fig. 3, in which the surface pressure F, and the surface potential  $\Delta V$ , due to the film are plotted against the weight of protein per sq. cm.  $\gamma$ . Some important differences are noticeable in the behaviour of egg albumen and glutenin as compared with that of gliadin. In the first place from the surface pressure curves it is seen that the compression needed to cause gelation of the film is much smaller, about I dyne per cm. in the case of egg albumen and glutenin, but ca. 15 dynes per cm. in the case of gliadin. From the surface potentials definite fluctuations in potential (> 5 mvs.) over the surface are apparent when the value of  $\gamma$  is less than  $0.6 \times 10^{-7}$  gm. per sq. cm. At any higher compression the film is electrically uniform as observed by moving the air electrode over the surface. Examined by the dark-field ultramicroscope the films are optically clear up to film collapse.



The gelatinous film is formed in all three cases at the same value of  $\gamma$ , about  $1.4 \times 10^{-7}$  gm. per sq. cm., but its compressibility is higher in the case of egg albumen and glutenin than for gliadin, while the change in electric moment from the liquid to the gel film is less marked.

There are two factors which may influence the ease of lateral compression of the fully expanded protein film. First, the actual length of the polypeptide chains in the respective proteins: for a long chain the probability of mutual separation of adjacent chains is correspondingly reduced, in a similar manner to the rise in the melting-point of a paraffin with the molecular weight. The molecular weights of egg albumen and of glutenin are about 34,500, while the most reliable value for gliadin is about 20,000.

The second factor to be taken into account is the degree of hydration of the peptide chains, which will depend largely on the polar or non-polar character of the various side chains, although hydration may also occur around the CO-NH peptide linkages. Compression of the

film to the close-packed gel structure would thus be associated with a

dehydration of the protein.

In these cases it is difficult to form an estimate of the nature of the side chains, the results of the hydrolysis of glutenin and of egg albumen accounting for barely one half of the molecule. Information as to the total polarity of the protein molecules perpendicularly to the surface

is, however, obtainable from the slope  $\left(\frac{d\Delta V}{d\gamma}\right)$  of the  $\Delta V/\gamma$  curves.

The value for gliadin is about twice that for egg albumen,  $3.2 \times 10^9$  as against  $1.5 \times 10^9$ , glutenin giving  $1.8 \times 10^9$  m.v./gm./sq. cm. These values refer to the most expanded state of film. That is, in the case of glutenin and egg albumen a much smaller proportion of the side chains contain a polar group such as COOH, OH or NH<sub>2</sub>. The degree of hydration will be proportionately smaller and the chains more easily compressible to the close-packed gel form.

# Myosin.

Some preliminary experiments with muscle globulin (from rabbit muscle) reveal the interesting feature that this protein will not spread to a film on water or on dilute salt solutions up to 1.8 per cent. NaCl. At a concentration of 2 per cent. NaCl however, spreading is rapid. Owing to the nature of the myosin extract obtainable it was impossible to estimate the weight per sq. cm. of protein on the film with any accuracy. At low compression the film was liquid, but could be compressed to a gelatinous film with a maximum surface potential of 300 mvs.

#### The Sol-Gel Transformation.

The existence of two characteristic types of protein film, the liquid and the gelatinous, made desirable a comparison with the change in surface properties associated with the three dimensional sol-gel transformation. Some experiments were therefore carried out with gelatin (Coignet) made up throughout in a M/IO sodium acetate acetic acid buffer at  $p_{\rm H}$  4.8.

The film spread on the surface of the buffer by the method of Gorter and Grendel was at 15° C. liquid and uniform in potential at an estimated weight per sq. cm. of about  $1 \times 10^{-7}$  gm., and became gelatinous at about  $2.5 \times 10^{-7}$  gm. per sq. cm. with a surface potential of 170 mv.s. The potentials increased with time, indicating an incomplete spreading of the protein initially.

Examination of the air-liquid potential differences for gelatin sols and gels of varying concentration gave the result shown in Fig. 4, in which the difference of the air-liquid p.d. from that of the pure acetate buffer

is plotted against the percentage gelatin.

At gel concentrations greater than I per cent. the value was approximately constant, but rapidly decreased when the concentration fell below about 0.5 per cent., which was the minimum concentration neces-

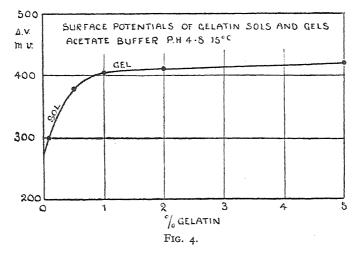
sary for gelation at the existing temperature (15° C.).

It was noticed in the case of the gelatin sols that the value of the surface potential obtained immediately after scraping the surface with a waxed glass slide was considerably smaller than the final value. Thus for a 0-01 per cent. sol the potential rose 80 mvs. in twenty minutes, and the process could be repeated apparently indefinitely. The same behaviour is well known in dealing with the surface tensions of colloidal

solutions (du Noüy *loc. cit.*), the observed increase of potential indicates a slow process of molecular re-adsorption and re-orientation in the surface layers after a disturbance. In the case of a gel at I per cent. concentration and higher, the surface orientation seems to be complete.

A further point of interest was noticed with regard to the setting point of the surface film as compared with that of the gel as a whole. The surface rigidity was observed qualitatively by the motion of talc particles placed on the surface. The surface of a gelatin sol possesses a definite rigidity, i.e. a talc particle blown aside gently will return to its original position, but only below a certain fairly well-defined temperature: 22° C. for a 0.5 per cent. sol, 25° C. for a 5.0 per cent. sol. The "setting point" of the surface film is about 2-3 degrees above that of the sol as a whole, while the process of setting is accompanied by a rise of potential of about 30 mvs.

It may thus be concluded that the process of gelation is associated



with an orientation of the protein molecules incipient in the surface layers of the sol.

The surface of the gelatin sol and gel was further examined in regard to the spreading thereon of other capillary active substances. It was found that dodecyl alcohol spreads rapidly on the surface of a gelatin sol, even on a 5 per cent. sol at 30° C. It will not, however, spread on a gel. Thus, an excess of dodecyl alcohol on the surface of a 2 per cent. sol at 25° C. produces an increase of surface potential due to the alcohol film of 100 mvs. On setting to the gel the original potential of the gel is regained, indicating that the alcohol film is no longer anchored to the gel surface in an oriented film. It may be suggested, therefore, that the surface of the gel is similar in nature to the close-packed gel structure of a surface film of gliadin or egg albumen. The exterior presented by such a surface is that of the residual side chains to the main polypeptide chain. These side chains may terminate in either polar or non-polar groups, with the result that the surface as a whole is not uniformly lyophilic and may indeed be lyophobic.

#### GENERAL DISCUSSION.

Dr. N. K. Adam (London), congratulated Mr. Hughes on his success in solving the difficult problem of spreading the proteins completely, and asked if he could say where the dodecyl alcohol has gone, when it apparently disappears from the surface as the gelatine solution gels.

Dr. J. R. Katz (Amsterdam) said: It may be interesting to compare the results of Mr. Hughes with gelatin with the results of X-ray work on the gelatinisation of gelatin. A mixture of equal parts of gelatin and water, enclosed in a glass tube with very thin walls (both ends closed) shows at 55° an amorphous X-ray pattern, at room temperature, the next day, a diagram containing crystal interferences.1 When gelatin gelatinises, the long chain protein molecules are laid parallel in each little gelatin particle which is formed out of the aqueous solution. But the axes of these little crystals lie at random. These gelatin particles must be rather long and must form a kind of felt during the gelatinisation.

Professor E. K. Rideal (Cambridge) said: One of the outstanding still unsolved problems was the structure of the two-dimensional gel state. It is evident that some definite change is taking place as the film is maintained in the gel state and that this change is associated with the formation of a linkage between the chains. If we denote the polar side groups by R and the ketoimido linkage by S, the linkage may be of the types RR, SS, or RS. The evidence, such as it is, suggests an SS linkage, but this cannot be regarded as certain.

Mr. W. T. Astbury (Leeds) said: I have no hesitation whatsoever in congratulating the author on this paper because his results agree so well with my own conclusions arrived at by a perfectly independent method, that of X-ray analysis! From a review of all the available X-ray data on protein structure,2 it appears that, when the protein main chain is in the extended state, each amino-acid residue is defined approximately by the three dimensions  $3\frac{1}{2}$  Å.,  $4\frac{1}{2}$  Å., and  $9\frac{1}{2}$  Å. The author postulates that when his films are in the "gelatinous" state, the side-chain dimension (9½ Å.) is normal to the surface. In this state, according to the X-ray arguments, a surface area of  $3\frac{1}{2} \times 4\frac{1}{2} \times 10^{-16}$  sq. cm. should contain one residue of average weight 120 × 10-24 × 1.65 gm., that is, I sq. cm. should contain  $\frac{120 \times 1.65 \times 10^{-24}}{1.00 \times 1.00}$ 

 $\frac{1.5 \times 10^{-16}}{3.5 \times 4.5 \times 10^{-16}} \approx 1.26 \times 10^{-7} \text{ gm}.$ egg albumin, glutenin, and gliadin, Hughes finds about  $1.4 \times 10^{-7}\,\mathrm{gm}$ . (roughly the same as the earlier value of Gorter and Grendel), which is in very satisfactory agreement with prediction. It should be pointed out, too, that Gorter and Grendel found similar results whether the proteins under examination had molecular weights, as determined by Svedberg, of 34,500 or two, three, or six times this value. It seems difficult, therefore, to resist the conclusion that these multiple molecular weights are built up by a mechanism of parallel orientation after the manner recently suggested.3

<sup>&</sup>lt;sup>1</sup> J. R. Katz, J. C. Derksen and W. F. Bon, Rec. trav. chim. Pays-Bas., 50, 725, 1138, 1931; 51, 513, 835, 1932.

2 See "Some Problems in the X-ray Analysis of the Structure of Animal Hairs and other Protein Fibres," p. 193.

3 W. T. Astbury and H. J. Woods, Nature, 127, 663, 1931.

# PART II.—FIBRE PARTICLES: THEIR PRODUCTION, DEFORMATION, AND DEGRADATION.

# CONTRIBUTION TO THE STUDY OF THE DEGREE OF RIPENING OF COTTON.

By OLIVIER ROEHRICH.

(Chef de Laboratoire au Conservatoire National des Arts et Métiers, Paris.)

Received in French on 24th June, 1932.

In stating this problem we cannot do better than reproduce the scheme of W. L. Balls. Balls has shown that, from the first day of its appearance above the tegument of the seed, the hair is a hollow cell of a circular cross-section which already possesses a definite maximum diameter; this latter is determined by the cuticle, which cannot be distended without bursting. This diameter is a character of the strain and is the more constant as the strain is the more pure. Little by little secondary layers of cellulose are deposited within the initial circumference, reducing the lumen in proportion.

The hairs, according to the conditions of growth and also, as Denham

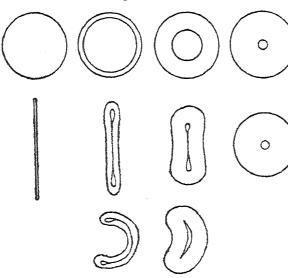


Fig. 1 (partly after W. L. Balls).

has shown, according to the compression in the closed boll, are more or less nourished, ranging from hairs which are but a primary membrane to those in which the lumen is almost obliterated.

From the moment when the boll opens, we notice from minute to minute, under the influence of the desiccation by the air and

sun, a flattening of the fibre, and the lumen from being wide open becomes squashed in.

Fig. I (after Balls) shows on the top line four fibres of the same diameter, that on the left reduced to its primary membrane, the second slightly thickened, the third normal, and finally the last over-nourished and with reduced lumen. The row below shows the form each of these fibres would take when the boll opened. We see that the more the fibre is thickened the less is the width of the ribbon; (note that the figure does not take into account the diminution in size due to the dessication of the cellulose, which makes the perimeter itself of the sections diminish, as has been shown by Calvert and Summers, the cuticle following closely, with folds, the new perimeter).

In cross-section the thin fibres often have a channel-like form, the normal fibres assuming a bean-shaped section, as indicated in the bottom

row of Fig. 1.

These considerations indicate, without further explanation, how difficult it is to ascertain the true diameter of a cotton by the observation either of sections or of the fibre viewed lengthwise. On the other hand if one could ascertain for a cotton its real diameter—a character of the strain—and the extent of its thickening, one would have a clear idea of its degree of ripening.

I. To Determine with Precision the true Diameter of a Cotton.— We have found in the literature but a single solution of this problem, a solution which we have for a long time used in our studies of cotton. This method, put forward by Calvert with Cross, Harland, and then Summers, is based on the original cylindrical form of the hair.

They have noticed that at 40° Tw. or at 25° Baumé the mercerisation of a cotton in a soda lye swells it throughout, untwisting the cuticle without burst-

ing it, making cell rethe assume original form which characterised it in the boll. Fig. 2, which we borrow from them, shows a normal ribbonlike fibre of

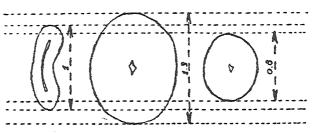


Fig. 2 (after Calvert and Summers).

diameter I; treated with NaOH of 25° Baumé this assumes an approximately circular form of diameter I·3, the same as that of the original cell, as these authors have verified. If the mercerised fibre is rinsed and dried it is reduced in diameter, but it retains its circular form; the diameter is now no more than 0·8.

2. To ascertain the Wall-Thickness of the Cotton Fibre.—The older workers, such as Yves Henry, judged the ripening by the convolutions, and by the microscopical aspect of the fracture, which is more ruptured and fibrillary in the ripe than in the immature fibre.

Herzog has given some very characteristic figures for less ripe and wellripened fibres, which permit a skilled operator to obtain some idea of the degree of ripening of a cotton by the microscopic observation of fibres viewed lengthwise. This, however, does not give us figures.

Balls then measured the *thickness of the cellulose wall*, obtaining figures of great precision, but requiring very carefully made sections; an operation somewhat lengthy and delicate.

Finally, Balls and many workers after him have applied the gravimetric method; the weight of the median centimetre of the fibre (the approximate density of cotton cellulose being taken as I·5) giving a very clear idea of the thickness of the wall, when one is concerned with the same kind of cotton.

Quite recently G. G. Clegg has studied the degree of ripening by observation under the microscope of fibres which are mercerised on the slide beneath a coverslip. Well-ripened fibres give a good mercerisation, becoming perfectly cylindrical although they are quite twisted in the raw cotton. Fibres which are dead or slightly matured, ribbon-like or only slightly twisted in the raw assume, on the contrary, a quite characteristic twist in soda. Certain fibres, with only slightly thickened walls, remain indecisive. The author bases her method on a statistical evaluation of the three kinds of fibres, the first two, readily discernible, being counted directly, the third being given by the difference from the total.

In this paper we shall avail ourselves of this new method.

3. Methods of Combining Various Expressions for the Diameter of the Fibre with those for Wall-Thickness to obtain a Numerical Expression for the Degree of Ripening.—Kuhn makes a number of cross-sections, draws their outline in a circle, and calculates thence the percentage of fibre in the circle. Dantzer and Roehrich have, however, repeated this method and have demonstrated its practical impossibility.

Fikentscher draws cross-sections and measures their perimeter. He draws a circle of equal perimeter, and calculates the percentage of the lumen according to the calculated area of cross-section of the cell-wall. This method is impracticable.

Morton and Clibbens put as abscissæ the mercerised diameters, and as ordinates the hair-weights per centimetre. According to the position of a cotton on this diagram they get a clear idea as to the degree of ripening of the cotton.

We ourselves ascertain the diameter by mercerisation, and reduce the figure obtained to that of the ribbon-like fibre in accordance with the data of Calvert and Summers. We calculate in addition the weight of 10 metres of fibre from the weight of the median centimetre. From the weight, P, divided by the density (standard 1-5) we deduce the area of cross-section S of the cellulose wall. From the diameter of the ribbon we deduce the area S' of the circle having this diameter.

The ratio  $\frac{S \times 100}{S'}$ , which we designate the coefficient of maturation, gives the percentage of cellulose included in a circle having the same diameter as the fibre. It is a perfectly definite index of the degree of ripening.

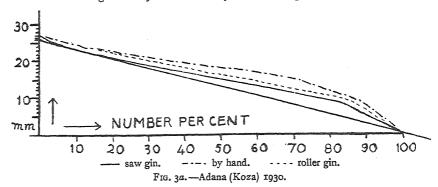
# A Practical Study of Two Types.

In order to demonstrate the precision and the convenience of our method of study we will show its application to two quite different cottons.

(I) An Adana Cotton (a Yerli-Koza) short staple of mediocre ripening, ginned on the roller gin, the bolls of this cotton do not open, and are picked entire; (2) A Pima cotton from the experimental fields in Morocco, of extra staple, well ripened, ginned on the roller gin.

To identify them we give in Figs. 3(a) and (b) their length diagrams,

obtained by using a Baer Sorter according to a gravimetric method we have already published. For the Adana, in addition to the full-line diagram representing the saw gin studied, we show the diagram of the same cotton ginned by hand and by the roller gin.



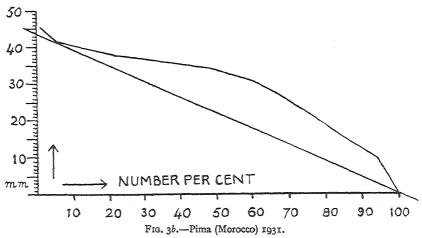


Table I gives some of the characteristics of these cottons, notably the weight per cent. of the short fibres and of the "neps" recovered

TABLE I.

		7.		
	Hand.	Roller.	Saw.	Pima.
Commercial length in mm	27·5 17·2 11·4	27·5 16·3 14·3	26 15 19·8	43 30·4 3·1

on the last comb, but omitting the coefficients of homogeneity which would require too long an explanation.

We note that the saw gin breaks the long Adana fibres which the roller gin leaves intact, and that the last comb is loaded not only with the short fibres, as in the case of the roller gin, but also with the "neps," as a result of which the weight of matter recovered rises from 11.4 per cent. to 19.8 per cent. The short statistical statement following, although only very approximate, clearly indicates that the "neps" are not preformed. We have counted in a gram of fibre the number of neps and of stars more or less formed at different stages of the picking, it being understood that we are dealing with cotton harvested in the boll, crushed and cleaned before being passed through the roller gin. The results obtained were—

We see that the "neps" arise, for the most part, from the action of the saws, at the expense of the cotton of a mediocre degree of ripening.

#### 1. Measurement of Diameter.

With this knowledge of the two cottons, we have sought to verify very rigorously the data of Calvert and Summers mentioned above. The diameter has been studied according to the three methods at a magnification of about 900 diameters.

(I) On the fibres themselves, without any treatment, mounted in 95° alcohol: we measured the widest portion of the fibre, that is to say the breadth of the ribbon; dead, untwisted, fibres which gave abnormally wide ribbons, were of course ignored. It must be remarked

that the personal equation enters here.

(2) By mercerisation between slide and coverslip at 25° Bé: we measured the diameter of the mercerised fibres, which were readily recognisable by their cylindrical structure; all which showed the least twist were neglected. As we made the measurements right in the middle of the field there was no hesitation as to whether the fibre was to be measured, even if it showed some bends. The vertical displacement of the movable stage of the microscope gave the place of measurement.

(3) By mercerisation of a tuft of fibre previously soaked in alcohol and pressed. It was rinsed, dried and then mounted in 95° alcohol. The measurement was carried out as by the other methods, but with more indecision, it would seem, in the choice of the fibre which has really

been mercerised than in case 2.

Table II gives the results obtained.

The observations of Calvert and Summers are therefore perfect. By dividing the mercerised diameter observed in soda by I·3, and the mercerised diameter washed and dried by O·8, we obtain almost exactly the diameter of the ribbon observed directly.

In each case the coefficient of variation is clearly better for cotton observed in soda (case 2), which indicates better readings in this case. The greater diameter in this method permits of more precise readings. Moreover, the really mercerised fibres can be distinguished with more certainty. This then is the method for choice in the study of cotton diameters, as it is the one which, in selection studies, will give the most rigorously exact coefficient of variation.

TABLE II.

	Untreated Fibre (Ribbon).	2. In NaOH.	3. Mercerised and Washed.		
Adana.  Mean diameter $(\mu)$ Calculated ribbon diameter $(\mu)$ Standard deviation Coefficient of variation	23·53 ± 0·21 23·53 3·88 ± 0·18 16·49 ± 0·98	$30.38 \pm 0.29  (\pm 1.3) = 23.36  4.39 \pm 0.21  14.46 \pm 0.82$	18.60 ± 0.20 (÷0.8) = 23.25 2.99 ± 0.14 16.12 ± 0.95		
Mean diameter $(\mu)$ . Calculated ribbon diameter $(\mu)$ Standard deviation . Coefficient of variation .	15·20 ± 0·13 15·20 2·05 ± 0·09 13·56 ± 0·76	20·52 ± 0·14 (÷1·3) = 15·78 2·17 ± 0·10 10·57 ± 0·56			

# 2. Gravimetric Study.

A second series of experiments was undertaken with the object of ascertaining with exactitude the weight of a given length of fibre. We cut from the median region of a bundle of fibres a length of 10 mm. of Pima and of 8 mm. in the case of the shorter Adana. Two hundred and fifty fibres were counted and weighed on the Huguenard microbalance. The operation was repeated five times for each cotton, so that the weight was obtained from 1250 fibres. The results in mgm. per 10 metres are given in Table III.

TABLE III.

Adana.	Pima.
2·52	1·51
2·63	1·56
2·56	1·63
2·26	1·58
2·42	1·55
M: 2·478	M: 1·566

Unless combined with the diameter these figures, as will be seen, give no idea as to the degree of ripening, the Adana at first sight appearing to have a greater wall thickness. Table IV gives for the two types

TABLE IV.

					Adana.	Pima.
Weight of 10 metres (P) in mgm.		•			2-478	1.566
Wall surface $S\left(=100 \frac{P}{1.5}\right)$ in $\mu^2$		•	•		165	104
Diameter of ribbon $D$ in $\mu$ .					23.36	15.78
Surface $S' = \frac{\pi D^2}{4}$ in $\mu^2$ .					428	196
Coefficient of maturation $C = \frac{S}{S}$	× 100 S'	as a pe	rcenta	age	38.5	53

this combination between diameter and weight as a coefficient of maturation.

In a circle of the diameter of the ribbon 38.5 per cent., in the case of Adana, and 53 per cent., in the case of Pima, is occupied by cellulose.

Hence there is a very wide margin for a numerical expression of the value of a fibre from the point of view of nutrition, whatever may be the kind of cotton studied.

# 3. Micrographic Examination.

It was interesting to know whether the inferiority of Adana was due to general malnutrition of all the fibres or whether certain fibres were sacrificed for the others; whether in the sample there were weak points due to particular bolls containing immature fibres, or whether the weak fibres were regularly spread through the sample. To this end the method of study of Miss Clegg has proved very useful.

The photomicrographs give (Fig. 4) a picture of Adana cotton mercerised between slide and coverslide and (Fig. 5) Pima cotton. It is seen that it is easy to distinguish the well matured fibres, mercerised throughout, the dead or very thin-walled fibres which show on mercerisation a quite characteristic compressed spiral. It is interesting to make observations in the polarising microscope with crossed Nicols. The dead and the quite thin fibres are almost invisible and the distinction is therefore the more easy.

One might imagine that the simple observation in a polarising microscope of a not mercerised cotton would suffice. This is not so; there are serious difficulties in separating with certainty the different kinds of fibres—as is shown in figures 6 to 8.

Fig. 6 shows an Adana cotton photographed dry—which explains the poor illumination. Certain well twisted fibres are manifestly ripe; as to others there is doubt. The two other photographs (Figs. 7 and 8) show the same point in the preparation after a drop of soda has been placed in the edge of the cover-slip. One fibre only, that which is curved, is well mercerised. A second which cuts across it at the bottom of the photograph has an imperfect mercerisation. All the other fibres are immature and have assumed a twist which readily differentiates them. Figs. 6 and 7 were taken with different angles in order to show all the fibres which, as will be noticed, readily become invisible.

We kept the slides which were used for measuring the diameter and counted, under a magnification of 250 diameters, the fully mercerised and the immature fibres as a ratio of the total number of fibres. The difference gives the indecisive, badly mercerised fibres with thin walls but having nevertheless a certain body. This calculation was made, field by field, until the whole slide had been covered. The results are given in Table V.

TABLE V.

		Adana. Per Cent.	Pima. Per Cent.
Mercerised Indecisive Immature	:	53•6 8 38•4	83·5 6·3 10·2

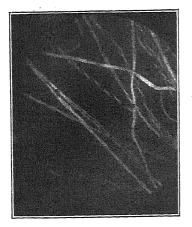




Fig. 4. Fig. 5.



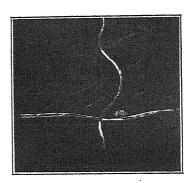


Fig. 7.

Fig. δ.

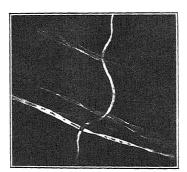
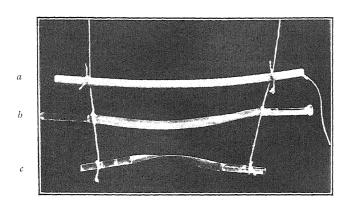


Fig. 8.

[To face page 224.



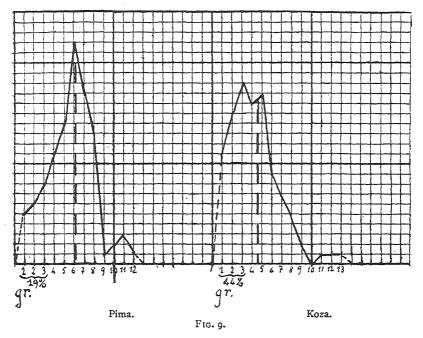
a. Stearin candle of about '5 cm. diameter, covered with gelatine. b. Gelatine pipe hardened with formaldehyde, filled with water, closed at both ends with a glass rod stopper. c. Same after drying, showing bandlike form and winding.

[See page 227.

In the case of Adana we found 34 per cent., 29 per cent., 46 per cent., 46 per cent. and 42 per cent. in the separate slides, which shows that the immature fibres are spread regularly throughout the sample. In the case of Pima, in two fields out of all the slides examined we saw once 28 per cent. and in the other 55 per cent. of immature fibres. In every other case all the cotton was entirely mercerised; clearly in this case certain bolls or certain seeds have immature fibres. The case, then, is quite different from that of Adana cotton.

# 4. Dynamometric Study.

We now sought to verify anew the manner of distribution of the immature fibres by a study of the tenacity of the cotton.



In the upper nip of an apparatus derived from that of O'Neill (the fibre dynamometer of Pontillon) we fixed a bundle of fibres from which we broke off 10. The operation was repeated ten times for each cotton. Table 6 gives the figures obtained in grams per fibre.

#### TABLE VI.

Adana	٠	٠	٠	•	3.45, 5.31, 4.38, 4.77, 4.49 Mean 6.54, 3.71, 4.29, 3.53, 5.52	1 4.599
Pima	•	•	•		7.52, 6.01, 4.46, 6.28, 6.87 3.89, 7.32, 6.07, 6.64, 6.95	ı 6 <b>·20</b> I

We see that for Adana the results are nearly constant, that is to say that strong and weak fibres are regularly distributed, whilst for Pima, on the other hand, there are two weak points at 4.46 and 3.89. which confirms the microscopic observation as to the presence of dead

fibres in packets.

The curves in Fig. 9 show that the true summit for Pima is 6 grams and for Adana 5 grams. If we suppose that the fibres which break at I to 3 grams are immature, we find 19 per cent. of the total for Pima, whilst microscopic observation gives  $10\cdot 2 + 6\cdot 3 = 16\cdot 5$  per cent. of immature or indecisive fibres, and 44 per cent for Adana-Koza, for which we see under the microscope 38.4 + 8 = 46.4 per cent.

Table VII shows the absolute strength of the cellulose of each of

the cottons.

TABLE VII.

	Adana.	Pima.
Tenacity of the fibre $(F)$ in grams. Weight of 10 m. of fibres $(P)$ in mgm.	4·599 2·478	6·201 1·566
Breaking Length in km. $L = \frac{10F}{P}$ .	18.55	40.80
Tensile strength in kg./mm. <sup>2</sup> $R = L \times 1.5$	27.88	60.75

As we see the differences are about double. Indeed we must consider not only the coefficient of maturation (i.e. the wall thickness) but also a quality of the cellulose bound up with the length and the fineness of the fibre.

The tensile strength per mm.2 is, roughly, proportional to the length and to the coefficient of maturation and inversely proportional to the diameter. If we write the empirical formula

$$R = \frac{L + C}{D}$$

we have for

Adana

$$R = \frac{27.5 + 38.5}{23.36} = 28.2 \text{ kg}.$$

Pima

$$R = \frac{43 + 53}{15.78} = 62.1 \text{ kg}.$$

which is sufficiently close to the 27.88 kg. and 60.75 kg. obtained experimentally. Without undue emphasis, this is only an approximation which may be subject to exceptions and comparatively large differences.

We believe that this method of very precise study will afford light on the knowledge of the cotton fibre. Practically it can serve to characterise the stage of maturation of a local crop, to control fertilising experiments, acclimatisation experiments, and selection or hybridisation in experimental fields.

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#### GENERAL DISCUSSION.

Miss Clegg (Manchester) said: With regard to the determination of the degree of ripening, the coefficient of maturation has certain disadvantages. It gives a general figure for the degree of thickening but not for the distribution. We have found that a cotton with a low maturation coefficient will give a strong yarn, but there is a tendency for the dead hairs (i.e., those with practically no secondary thickening) to nep up and spoil the appearance. Therefore from the spinners' standpoint a test which will distinguish the thin-walled and dead hairs and therefore give a measure of the potential neppiness of the cotton is probably of more value.

It does not appear possible to obtain this from the breaking load curves. We cannot assume that the weak hairs are necessarily immature. The low breaking load of many of the hairs is due to abnormalities and cracks in the wall which are particularly characteristic of the thicker walled cottons-the 44 per cent. of the Adana Koza said to be immature probably contain a considerable proportion of such hairs. The Pima, however, is a finer cotton and the breaking load will show a fairly good correlation with the wall thickness.

Professor P. Krais (Dresden) said: The distinction between dead and unripe cotton, as made by Alois Herzog, should be kept in mind. As to the bandlike windings of the cotton hair, I have made some experiments in order to investigate, whether the drying up of a plastic pipe filled with water will give the same formation. Indeed, a pipe of about 0.6 cm. diameter made of gelatine, hardened afterwards with formaldehyde, then filled with water and closed at both ends by a glass rod stopper, takes the same form of bandlike windings, when allowed to dry at the open air.1

Professor Roehrich, in reply, said: The communication of Dr. Peirce 2 shows quite well the differences of the point of view of the technologist, for whom the unit of cotton is the hair, and of the colloid chemist, for whom "the cell structure has been an unwanted complication in the study of cellulose in terms of molecular units." Miss Clegg has criticized my proportionality between the strength of the hair and its coefficient of maturation, specially for the coarse cottons, such as Adana. The data given by Peirce show really that hairs are frequently seen breaking at an abnormal point. The conclusion is that it would be

<sup>2</sup> See plate facing page 225.

<sup>&</sup>lt;sup>1</sup> Cf. Wiesner, Rohstoffe des Pflanzenreichs, 502, 1927.

better, in order to judge the strength of a cotton and the quality of cellulose, as independently as possible of the structure, to break the fibres in millimetre lengths, and not in centimetre lengths, as usual.

# THE MODIFICATION OF NATURAL COTTON CELLULOSE BY SWELLING AND BY DEGRADATION.

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The chemistry of cellulose is complicated by the fact that the material is capable of continuous modification in various ways, so as to yield an infinite number of products whose properties vary within wide limits. On this account, qualitative tests are of little value in the investigation of modified celluloses.

The study of the modification of natural cellulose has been carried out with the aid of a number of quantitative chemical and physical tests, whose interpretation is as a rule arbitrary and subjective rather than definite and stiochiometric. On the Continent there has been a general tendency to study relatively severe degradation of cellulose; in this country, particularly in the work of the Cotton Research Association, much milder treatment and relatively slight changes have been the object of attention. The present paper is chiefly based on results obtained by the second method of approach, which might be obscured by more drastic modification of cellulose.

The purpose of this communication is to show that cotton purified by a dilute alkali boil is a material of more or less definite chemical properties, and to indicate the essential lines along which this material may be modified.

By the action of swelling agents, activated products are obtained which display to a greater extent the same kinds of chemical reactivity as the original material, but the action of acids or of oxidising agents gives rise to "degraded" products characterised by essentially new chemical properties. The distinction between the two types of change—which often occur together—is best illustrated by assuming that natural cotton cellulose is built up of almost continuous lengths of units linked by primary valence, rather than of discrete brick-like units or "micelles." Whilst avoiding too definite a picture owing to lack of evidence, it may be assumed that in the "activated" materials the hydroxyl groups are more accessible or less mutually condensed in a transverse direction, whilst in the degraded products some of the glucosidic oxygen links which bind the material in an axial direction have been broken.

### Scoured Cotton Cellulose-a Uniform Product.

The hairs on the seed coat of the cotton plant contain—apart from moisture—about 95 per cent. by weight of the rather ill-defined substance cotton cellulose. This material is obtained in a more or less arbitrary

pure state by boiling the cotton hairs with caustic alkali. Milder cleansing agents, such as organic solvents, which are less likely to modify the cellulose itself, fail to remove the whole of the naturally occurring impurities. The alkali boiled or scoured cotton cellulose exhibits almost uniform properties, practically independent of the source or variety of the cotton and of the severity of the boil. It is characterised by a very low copper number (of the order 0.01),7 a high intrinsic strength, a uniform power of absorbing moisture 25 or dilute caustic alkalis, 17, 18 a uniform rate of reaction with mineral acids 22 or with alkaline potassium hypobromite.2 It also shows a high viscosity in cuprammonium solution, but this property is exceptional in that it varies largely according to the conditions of the alkali boil.12 Indeed, in the manufacture of nitrocellulose the viscosity of the nitrated product is controlled by the severity of the initial alkali boil. Such variations, as result from alkali boiling occur, however, in the region of high viscosity, where this property is an abnormally sensitive index of the smallest chemical modification of cellulose. With the exception of this property it is fair to state that alkali boiled cotton cellulose approximates closely to a definite chemical individual whose properties are independent of the variety and origin of the cotton and of the conditions of the dilute alkali boil.

It is not possible to say how far this purified substance has of itself been modified in the process of purification. It yields a less viscous solution than the original raw cotton, and it cannot be decided whether the higher viscosity of the latter is due to the presence of the impurities or whether in the alkali boil some of the primary valence bonds of cellulose are broken. It is known that boiling alkali causes rapid degradation in presence of oxygen. It might be inferred from the extremely low copper number of alkali boiled cotton cellulose that reducing glucose end groups are absent in the natural material, but it must be remembered that Clibbens and his co-workers 4, 7 have shown that alkali boiling destroys the reducing power of all chemically modified celluloses. appears, therefore, that the exact chemical state of natural cotton cellulose is likely to remain rather obscure until some milder process of purification is available. The properties of this scoured cotton cellulose -uniform with the exception of viscosity in cuprammonium-may be modified as a result of chemical treatment along two directions which are quite distinct, by swelling and by degradation.

It is perhaps unfortunate that many reagents bring about both these types of change, because on this account some confusion has arisen and their essential difference may be obscured.

# Swelling and "Activation" of Cellulose.

Certain reagents under suitable conditions of temperature and concentration cause cotton hairs to swell or expand greatly in diameter by imbibition of the liquid phase, whilst the length of the hairs contracts.

These reagents are aqueous solutions of:

- (I) Caustic alkalis, whose mode of action 16 is probably
  - (a) formation of ionised salt;
  - (b) attraction of the solvent by osmosis.

These are most effective at moderate concentrations and low temperatures.

(2) Hygroscopic substances, such as sulphuric acid, zinc chloride, calcium thiocyanate—most effective at high concentrations and high temperatures. (3) Specific substances such as cuprammonium hydroxide or caustic soda—carbon bisulphide. By washing with water the swelling agents may be wholly removed from the swollen cellulose and the resulting material dried. It is found to possess the same empirical formula  $C_6H_{10}O_5$  and to display the same chemical properties as the original cellulose, but to an enhanced degree.

The measurement of its specific volume "by immersion in helium, water or toluene, shows only a very slight increase, of the order of I per cent. X-ray examination indicates that a certain rotation of the glucose residues has taken place, but in some of this work the importance of constraint or freedom in the shrinkage of the fibres has perhaps been overlooked.

Cellulose which has been swollen or activated shows no entirely new properties, such as would indicate the appearance of reducing sugar or carboxylic acid groups. It does not show a sensibly higher specific volume in any immersion medium, indicating that it is not permanently swollen. It may be given the name "activated cellulose," though this name is not ideal. The meaning to be conveyed is that of increase of active mass rather than elevation to a higher energy level, increase in quantity but not intensity of reactivity. The degree of activation increases with the severity of the swelling treatment, e.g. with the concentration of the caustic soda up to 15 per cent. in "mercerisation". The activation, which results from treatment with caustic soda, is a maximum after the material has been washed with cold water and dried at a low temperature, it is decreased if restraint is applied during the swelling process so that the hairs do not shrink freely, or if they are restretched after the shrinkage has occurred. The activation is less if the alkali is washed out with hot water or with brine instead of with cold water, and is reduced if the material is dried at a high temperature. 18, 17, 2, 26

The complete solution of cellulose—as in the manufacture of rayon—represents a treatment more intense than mere swelling, but of the same type, and so we find that regenerated celluloses are more highly activated than cotton which has merely been swollen. All technical rayons, however, have also suffered degradation due to oxidation processes, so that, as will be seen in the sequel, they represent, relative to natural cellulose, a material which has undergone both types of change—"activation" and "degradation".

The activation of cellulose is indicated by the enhancement of the following properties, which are in a less degree characteristic of the scoured natural cellulose itself.

(I) Absorption of water vapour.26, 2

(2) Absorption of NaOH, 17 Ba(OH), 18 or cuprammonium hydroxide 5 from dilute solution.

(3) Copper number after a standard treatment with boiling 5 per cent. H<sub>2</sub>SO<sub>4</sub>.<sup>22</sup>

(4) Copper number after a standard treatment with dilute alkaline potassium hypobromite.<sup>2</sup>

Characteristic values of these quantities, after swelling treatments of various kinds, are given in the table.

It will be noted that the ratios which express the activation relative to natural cellulose are not independent of the indication which is chosen, thus, for example, mercerised cotton is not equally activated towards water vapour and towards barium hydroxide.

TABLE.

Properties which Change with "Degradation" of Cellulose.

Properties which Increase with Swelling or "Activation" of Callabse.

	Teosile Strength	Fluidity in ors per cent.	"Copper No." (Braidy). Gras, Cu refused by	*Absorption of Nethylese Blue	Abso. of Water goos.jgm. at 50 Per Cent. Relative	Absn. of NaOH from N/z Solution.	Abso. of Ba/OH <sub>a</sub> ) from N/5 Solution.	Rise in Cu No. Schwalbe) after 15 Mins. in Rei ling 17 me anni	Cu No. (Braidy) after 2 Hrs. in N/10 KOH, N/10 KBrO at 18° C,	Aloso, of Sky Blue FF Direct Dyel at 100° C.	Reference Numbers.
	dynes/cnik	Solution.	100 Gus, of Celubric	(Basic Dye).	Humidity,	Milli-Equivalents	per Glacose Unit,	Bolling 5 parcest. H <sub>B</sub> O <sub>b</sub>	at 18°C,	inner nýsi se rou cr	
Natural cotton cellulose scoured with 1 to 2 per cent.  NaOH under to to 40 lbs, log in, pressure  (Treated HCl 200*)1. for 24 bours at 20°C.		1.5	0.02	03 to 08	0°055 Ratios. 0°97	42°5	71 Ivsis or oxidation of	212	I'Ş	o 15 per cent.	19, 4, 12, 7, 25, 17, 18, 22, 2
"Degraded Ordines of the Landson of the Control of the Control of the Control of Control	2.4 X 10 <sup>8</sup>	***	2°44 0°5 3°4	3'0 I'I	097	the cellulose. (See		dation of cellulose, degradation.   See	idated by great degra- but unaffected by mild ref. 2).		12, 4, 17, 18, 2, 27 4
Treated 25 per cent. NaOH without restaint on swelling or shrinkage, weaheld, air dried "Activated "As above, but without allowing shrinkage cellulose Treated without shrinkage, but dried at 110° C. Swellen in 6570 per cent. H <sub>2</sub> SO <sub>4</sub> without restraint (time of action, 5 mins)			unaffected by swelling cellulose.	or activation of	1°50 1°35 1°2 1°83 (max).	Esp 2°55 1°96 1°89 3°20	essed as Ratios Relative 2º70 2º05 1º99 3º20	to Scoured Critica.	145 145 145 254 (max.)	18	6, 12, 7, 4, 26, 3, 8, 17, 20, 2 26, 17, 2 26, 17
Callulose Viscose rayon	About 4 X Io <sup>9</sup>	40 28	05		20 184	3% 34	4°0 3°8	5 5		0°9 2°9	28, 29, 21 28, 17, 18, 21
Reference Nos.	19, 12, 6	9, 4, 12, 21	4, 6, 21	3, 4	27, 25, 2, 26, 28	17	IŜ	22	2	29	

The authority for any given figure is that reference which appears at the end of both the horizontal and vertical columns, except in certain obvious cases where the vertical column number alone suffices.

\*The interpretation of this test is complicated by the fact that the variation of the p<sub>a</sub> affects the absorption by different modified celluloses in quite different ways.



Properties which are sensitive to "degradation," such as tensile strength and viscosity in cuprammonium solution, are not appreciably affected as a result of treatment with swelling agents, so long as oxidation or acid hydrolysis are avoided.

# Hydrolysis and Oxidation-"Degradation" of Cellulose.

By the action of acids or oxidising agents, cotton cellulose is irreversibly modified in such a way that its intrinsic strength and viscosity in cuprammonium solution fall. The modification of cellulose by acids appears to follow a definite course which is independent of the conditions of acid treatment, but the rate of modification depends on the hydrogen ion activity and on the temperature. Such a result must be expected from analogy with the sugars.

The oxidation of cellulose is, on the other hand, like that of the sugars, a more complex process. The course of the oxidation depends essentially on the nature of the oxidising agent and, although there is a general tendency for the formation of aldehydic or reducing "oxycellulose" in acid solution, and of carboxylic or acidic "oxy-cellulose" in alkaline solution, it is not possible to make any strict generalisations.

The loss of strength and fall in viscosity which accompany the hydrolysis or oxidation of cellulose are quite irreversible, and the general term "degradation" is commonly applied to these changes. The degradation of cellulose is accompanied by the appearance of chemical properties foreign to the original material. The hydrolysis of the glucoside oxygen bridges causes the appearance of reducing sugar properties which may be quantitatively though arbitrarily assessed as "copper number" or "iodine number". These reducing sugar properties also arise as a result of oxidation and may be accompanied by the development of a pronounced acidic reactivity, so that oxidised cellulose may strongly retain traces of caustic alkalis or absorb basic dyes. This latter property has been put on the quantitative basis which is so essential in the chemistry of cellulose, in the form of the "methylene blue absorption test." 8, 3

In contrast to these new properties which arise from degradation of cellulose, it is found that the chemical properties characteristic of the original material, such as absorption of water and of moderately dilute alkalis, are not seriously affected.

"Degradation" and "activation" represent therefore, quite distinct types of modification of the original cellulose, although in certain reagents such as 70 per cent. sulphuric acid both changes are effected side by side. Again in the manufacture of rayon the intense swelling and dissolving action leads to an "activated" cellulose, whilst the oxidation which is used to reduce the viscosity of the solutions is such as to provide a large measure of "degradation."

In the table an attempt has been made to collect data which illustrate the effects of a few typical actions on the chemical properties of cellulose. It is intended that this table should be self-explanatory, and that it should demonstrate clearly the essentially independent existence of the two main types of modification of natural cellulose.

#### Theoretical.

The modification of cellulose is so complex a subject that generalisations and conclusions of a theoretical nature should be made with extreme

aution. It is generally considered that cellulose fibres are built up of eparate rod-like bundles of primary valence chains and these bundles are commonly called "micelles." Whilst it is probable that there is in some degree closer association amongst the members of certain groups of primary valence chains, so that when the cotton hair is torn a ropeike structure appears at the break, there seems to be no conclusive evidence that the primary valence chains are not in the natural cellulose quite unbroken. The supposition, largely based on X-ray evidence, that certain reactions occur on the surface of "micelles," should not be accepted without close examination. The existence of such surfaces of discontinuity in the interior of the fibre is a matter which still lacks definite proof. The effects described in the present paper can be explained on the basis of a structure more or less continuous lengthwise, held together transversely by the operation of secondary valence forces between the polar hydroxy groups and oxygen atoms. Swelling causes a separation of the hydroxy groups which is only partially reversed on drying so that "steric hindrance" is reduced and the reactivity generally is higher. It seems unnecessary to make th emore definite assumption of any subdivision of "micelles" as a result of mercerisation. It may be assumed that the liberation of hydroxy groups occurs without breaking the glucosidic oxygen bonds which hold the structure in a lengthwise direction, so that the tensile strength and viscosity in cuprammonium solution are, as has been shown, unaffected.

The action of acids or of oxidising agents is of quite a different type. It results in the breaking of the axial primary valence oxygen linkages, so that reducing properties arise owing to the production of free aldehyde groups, the tensile strength and viscosity fall, whilst the types of reactivity due to the normal 2.3.6 hydroxy groups remain at much the same level. Several attempts have been made to calculate from various properties the average length of the unbroken primary valence chain in a given sample of cellulose. Staudinger 24 relys chiefly on the viscosity of dilute solutions of cellulose; Freudenberg 13 has used the optical rotatory power and the "iodine number," Mark 15 the method of X-ray analysis, Stamm 23 the super centrifuge, Haworth 14 the method of exhaustive methylation. In no case, however, is any definite interpretation of the results wholly free from criticism, and the estimation of the "molecular weight" must be regarded a somewhat arbitrary process whose utility in harmonising a complex mass of experimental evidence has yet to be shown.

The facts which are summarised in this communication do not necessitate the assumption of a structure consisting of "micelles" or quite definite separate units intermediate between the glucose residue and the cotton hair as a whole, nor does it appear that such an assumption is of real value. A discontinuous "micellar" structure does not explain so naturally phenomena such as the axial shrinkage and great lateral swelling without dissolution in solutions of swelling agents, and the great restraining effect of axial tension on such swelling. It necessitates a rather arbitrary distinction between inter- and intra-micellar reaction. Thus Craik and Miles 10 have shown that in the fractionation of nitrocellulose from aqueous acetone fractions are obtained which differ in viscosity, i.e., chain length, but not in degree of nitration, whilst Birtwell, Clibbens and Geake have shown that in the case of "oxycellulose" fractions differing in degree of oxidation may be obtained. It may be assumed that the reactions occur at random throughout the interior or

merely on the surfaces of "micelles," and it may be assumed that in the solvents the "micelles" either remain whole or split up into separate primary valence chains. On the micellar theory the two facts cannot be reconciled without supposing that a different mechanism is operative in the two cases of nitration and of oxidation unless it be supposed that oxidation itself reduces the micellar size. Such a change is, however, usually regarded as the underlying cause of the "activation" of swollen celluloses, which is essentially quite distinct from the process of oxidation.

No such confusion arises if it be supposed that nitration and oxidation both occur more or less at random in a structure which, though imperfectly crystalline is continuous except for random breaks in the primary valence chain. In the fractionation by solvents the longer chains aggregate and come out of solution most easily so that in any event the separation is by "chain length" or viscosity, and chains of different lengths, having been nitrated in a random fashion, show the same average nitro content. In the case of oxidation, on the other hand, the frequency of oxidation and the chain length are interdependent.

It is evidently necessary that a theory of cellulose structure should give a clear picture of the distinction emphasised in this paper between the types of modification, and it is suggested that the "micellar" or discontinuous theory is lacking in this respect. The assumption that the structure is continuous but slightly imperfect gives a natural explanation of these changes, "degradation" consisting in the completely irreversible breaking of the longitudinal primary valence bonds, and "activation" in the partially reversible separation of hydroxy groups bound together by secondary valence.

The nature of the X-ray diagrams obtained from cellulose fibres seems to preclude the possibility that the variations from a perfectly crystalline structure are purely random. This observation can perhaps be brought into line with other evidence by the assumption that in the structure of cellulose there is a rhythmic variation from the perfectly crystalline without sharp discontinuities.

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<sup>25</sup> Urquhart and Williams, J. Text. Inst., 15, T138 and 433, 1924; 17, T38,

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<sup>28</sup> Urquhart and Echersall, Shirley Inst. Mem., 11, 75, 1932.

29 Tentative results of work in the author's laboratory.

#### GENERAL DISCUSSION.

**Professor H. Mark** (Wien) said: I would like to point out that the word "micelle," which was used so frequently during this meeting, is a very old one and was first applied by Naegeli for a botanical and morphological purpose. When we extend its application to colloidal solutions we have to be aware, that there might be a certain change of its content. As far as we know by the optical investigation (birefringence and X-ray analysis) of cellulose and its derivatives there must be a certain amount of well-orientated matter in these fibres or films. These oriented parts —the so-called micelles—must be separated from one another by walls or partitions of a different character. It may easily be imagined that these separating parts consist also of main valence chains of glucose units, which are less oriented or even less regularly built up.

While the crystallised part of a fibre has been fairly well studied, we know nearly nothing about the intermediate substance. There is much evidence for the assumption that the technical properties of a given material depend to a very high degree on this amorphous amount, and I agree with the technical members of this meeting that we do not know very much about these special things, although our general know-

ledge of the structure of cellulose may be very much increased.

Professor H. Staudinger (Freiburg i. B.) (communicated): Professor Mark has been dealing with the question of the micellar structure of celluloses, especially on the basis of the micellar theory of K. H. Meyer and H. Mark, which has given rise to much discussion in recent times. This micellar theory has arisen in the following manner. C. Nägeli realised that cellulose and other natural products are crystallised and thus designated their little crystallites as "miscelles." Hence, Nägeli's micelle is identical with a crystallite. This particular term is only applicable to the solid state. As to the colloidal solutions of cellulose derivatives, in recent years colloid chemists commonly assumed a micellar structure of the particles. Thus, McBain noticed that certain relations exist between the solutions of cellulose-nitrates and soaps. Since a micellar structure had been proved for the colloidal particles of soaps, it could be well understood that the colloid particles of cellulose and rubber would have a similar structure too. K. H. Meyer and H. Mark now believed they could prove that the micelle in the solid state is of the same order of magnitude as in the dissolved state. They determined the size of the crystallites from X-ray diffraction and assumed on the basis of the investigations of R. O. Herzog, the identity of the crystallites with the micelles in the solution. According to these investigators the colloid particles of cellulose solutions are so built up that relatively short primary valence chains associate, on account of strong intermolecular forces, to govern the micelles.

Now, from the investigation of synthetic high polymeric substances it was ascertained without any fear of contradiction that such substances consist of long molecules when in solution and that the colloidal nature

of the solutions is conditional upon the lengths of the molecules. The relations between soap solution and cellulose solution, noticed byMcBain, arise from the fact that long molecules are present in both the soap solution and in the cellulose solution. Thus the shape of the particles is responsible for the colloidal nature of the solution. On the other hand it is not possible, without further suppositions, to derive the structure of the particle size from the colloidal properties of the solution. This will not be possible until a chemical investigation has been carried out on the basis of a polymerite-homologue series.

Thus the old conception of rubber and cellulose proves to be correct, namely that they are really high-molecular in the sense of the old classic organic chemistry. Future work in this field requires the intensive co-operation of organic chemistry, colloid chemistry, and physical chemistry. Then we may hope that the complicated problems of the

structure of high-molecular natural products will be solved.

Professor H. Mark, in reply, said: The present investigation was confined to artificial fibres in the solid or slightly swollen state. In this case there is no doubt that we have to deal with micelles or little crystals, which are distributed at random at the beginning and orientated at the end of the extension curve. Double refraction and X-ray patterns prove their existence. As to the question of the existence of particles in the solution we shall have the pleasure of hearing some very interesting contributions to this problem, so that it might be preferable to discuss this point later (see p. ).

Mr. R. J. Hannay (Bollington) said: It has been pointed out in Mr. Neale's paper that the general reactivity of cotton cellulose is increased by treatment with caustic soda and swelling agents having a similar action, and one of the manifestations of this increased reactivity is in the increased absorption of substantive dyes. This is particularly noticeable in the dyeing industry when a fabric woven from a cotton warp and viscose rayon weft is dyed under normal conditions, then the viscose weft always shows a darker dyeing than the cotton warp.

This can be explained by the increased reactivity of the viscose cellulose due to the swelling action of the caustic soda and carbon disulphide in manufacture. A further explanation has been advanced by Professor Mark 1 on the basis of de-orientation of the micelles in the viscose giving greater inter-micellar space and thus allowing a greater absorption of dyestuff, Mark's theory being that the dyestuff does not actually enter the micelles but only occupies the space between them. Both the above theories give a very reasonable explanation of what occurs in dyeing a fabric woven from an unmercerised cotton warp and viscose rayon weft. Under normal dyeing conditions a fabric such as the above in which the viscose rayon is replaced by cuprammonium rayon would behave in a similar manner. The difference between the weft and warp would probably be more marked in this case due to the greater affinity of cuprammonium rayon as compared to viscose (compare Neale's paper, last column of the table showing absorption of sky blue).

It is not widely known, however, that by using the same substantive dyestuffs under certain controlled conditions a reversal of the absorption can be obtained in the case of cotton and viscose rayon. Thus it is quite possible to dye the cotton warp much darker than the viscose

<sup>&</sup>lt;sup>1</sup> J. Soc. Dyers and Colourists, 48, 55, 1932.

weft, but curiously enough a fabric woven from a cotton warp and cuprammonium rayon weft does not show this effect at all, and the result in this case is the same as that given under normal conditions. It might be pointed out that the viscose rayon is not "stretch spun" whilst the cuprammonium yarn is "stretch spun." If, however, you take a "stretch spun" viscose rayon such as Lilienfeld yarn and dye it under the same controlled conditions it behaves in the same manner as the ordinary viscose rayon, and not like cuprammonium rayon. On the other hand a hydrolysed "acetate rayon" acts in the same manner as cuprammonium rayon.

The above effects are not explained by either the activated cellulose theory or by Mark's orientated micellar theory, and it is fairly evident that other factors greatly influence the absorption of dyes by cellulose fibres. Neale draws attention to the last column in the table at the end of his paper in which it is shown that viscose rayon shows less absorption of sky blue F.F. than cupra rayon and also less than activated or mercerised cotton cellulose which bears out in part the experiments mentioned, but it must be pointed out that the cotton yarn used for the warps in the fabrics taken for the experiments was not mercerised and was, if anything, more lightly treated than his natural cotton cellulose shown in the top horizontal column of the table. Cotton cellulose so treated shows a much smaller absorption of sky blue F.F. than viscose rayon, yet it is quite possible to dye the cotton much darker than the viscose in the same dye-bath if carried out under controlled conditions, and using sky blue F.F. as the dyestuff.

**Dr. J. R. Katz** (Amsterdam) said: Like Professor Mark I want to emphasise the importance which may be attached to the new form of the micellar hypothesis which Mr. Neale has developed in his paper and which I have found approximately in the same form in other

papers, for instance, in that of Mr. Astbury.

Two facts speak in favour of this hypothesis. In the first place, it explains the cohesion of a solid which swells; although liquid penetrates between its small particles (micellae or molecules) it keeps its cohesion, although this is lessened.2 We know that substances showing real swelling are almost always substances of a high molecular weight,3 possessing according to modern conceptions molecules in the form of long threads. The fact that cohesion does not get lost when liquid penetrates into the interior of a swelling body is perhaps the most surprising fact we know about swelling. A precipitate of barium sulphate, for instance, does not swell, does not show this cohesion. Why then does every precipitate of cellulose, of starch, of proteins, exhibit swelling and cohesion? Mr. Neale's hypothesis may explain it: because the parts of looser structure between the really crystalline spots called micellae may bind these micellae together. Such looser parts are present—according to modern work of Smekal and others—even in all ordinary crystals, even in clear pieces of rock salt. They may be more developed in the case of long chain molecules. I may add that I myself have always felt a certain doubt in drawing from an unchanged X-ray diagram the conclusion of intermicellar swelling.4

<sup>&</sup>lt;sup>2</sup> See my paper on the "Laws of Swelling," under paragraphs 1 and 11, pages 279 and 293.

<sup>3</sup> Ibid., under paragraph 2, page 280.

<sup>5</sup> Ibid., under paragraph 2, page 280.

<sup>6</sup> Fundam prakt Nature. 3, 365, 1924; in

<sup>&</sup>lt;sup>4</sup> See *Physikal. Z.*, **25**, 661, 1924; *Ergebn. exakt. Naturw.*, **3**, 365, 1924; in later years I have not expressed these doubts so explicitly, because nothing seemed to confirm them.

Secondly, the phenomena observed in the stretching of rubber 5 point in the same direction. Suddenly, at an elongation of 75 per cent., many minute submicroscopic crystals appear in a substance which showed an amorphous pattern before; the more strongly one stretches, the more "crystals" appear. Are these "crystals" units which pre-existed in the unstretched rubber as units sharply divided by an interspace from one another? This does not seem a very probable hypothesis. The X-ray evidence about the structure of liquids forces us to believe that they are built up from little groups of molecules lying parallel. These groups are, in the case of liquids, certainly not divided from one another by clear interspaces. If we accept the same conception in the case of amorphous rubber, and if such a group, in getting a three-dimensional order, gives crystalline interferences, must we then assume that it suddenly breaks, with a clear interspace, from the adjacent groups?

If we accept the new form of the micellar hypothesis, X-ray work on swelling will have to find a new interpretation. If an X-ray diagram remains unchanged during swelling, we can only conclude that the many little islands, where the structure is strictly crystalline, do not change in their internal structure. But between these little islands there may be places where the molecule chains are lying less densely packed, where a solid solution is formed: a dispersion of the liquid between the molecules of the solid. The same reservations would have to be made in the interpretation of the diagrams which up to the present were explained as intramicellar or as permutoid swelling. Swelling would then be far less a phenomenon of surface-adsorption than is mostly accepted in colloid chemistry. I may be allowed to recall that as early as 1910-1917 I compared swelling with solid solution, emphasising the importance of the solution hypothesis 6 at a time when every one else explained the phenomenon by surface-adsorption.

It may be interesting in this connection to remember that many substances—such as starch and agar-agar—which do not show any change in their crystalline X-ray pattern over a large range of vapour pressures, do get an amorphous X-ray pattern when dried carefully. This fact suggests that even those crystalline X-ray diagrams which have not shown any change, when the substance was dried (cellulose, chitin, for instance) may show a small change when the drying is very careful and if the methods of measurement are very exact. Small changes of this kind have been observed, but the phenomenon is still being studied.

Mr. Neale, in reply, said: In my opinion a structure for natural cellulose fibres consisting entirely of main valence chains is in better accord with technical experience of the properties of the fibre—such as shrinkage in length on swelling in alkali—than a structure in which more or less discrete brick-like units or micelles are linked by an amorphous cementing substance. At the same time the broadening of the spots in the X-ray pattern indicates there are regularly recurring areas of good and bad orientation-random imperfections in a large single crystal would merely cause a weakening of the spots. The X-ray evidence could be brought into line with technical experience by

<sup>&</sup>lt;sup>5</sup> Naturwiss., 13, 411, 1925; Gummi-Zeitung, 41, Nos. 36 and 37, 1927.
<sup>6</sup> Gesetze der Quellung, Koll. Beih., 9, 1, 1917; Z. Elektrochemie, p. 800, 1911.
<sup>7</sup> Starch, Z. physik. Chem. 150A, 100, 1930; Agar-agar, Recueil trav. chim. Pays-Bas, 51, 513, 1932.

assuming that good and bad orientation recurred without sharp discontinuity in a rhythmic manner in the fibre, the areas of bad orientation consisting—at any rate in the natural fibres—merely of long main valence chains displaced from the perfectly crystalline position. Such displacement is, as Mr. F. T. Peirce had pointed out, a highly probable occurrence in the growth of cotton hairs.

In exact work on cellulose, which is not a chemical individual, far too little attention has been paid to the necessity of a most exact description of the origin, purification and properties of the samples used. It is possible that the true direction of progress lies not in the determination of a particular molecular weight but in the correlation of the molecular weights of variously treated samples of cellulose with their pre-treatment and with the exact empirical tests which are in technical use.

On this account I would suggest that the following description should be given of any sample of cellulose used in laborious or exact fundamental work:—

(1) Botanical variety and species of the natural raw material.

- (2) Exact details of method used in purification (alkali boil, bleach, etc.).
- (3) Viscosity in cuprammonium hydroxide at a standard concentration.8
- (4) Reducing power or "copper number," the best technique being that of Heyes.9
- (5) Reactivity test against a standard reagent, the most exact and simple test being the absorption of baryta from N/5 solution. These tests are unfortunately not stoichiometric, but they are easily carried out and give exact results which serve as an empirical definition of the sample of "cellulose."

In regard to the question of dyestuffs absorption, it is difficult to interpret the quantitative work which has so far been done on this problem, on account of the large number of factors which have been varied simultaneously.

In my laboratory we are making exact measurements of the absorption of pure dyestuffs on cellulose sheet, under conditions such that only one factor—time, salt concentration, dye concentration, temperature and so on—is varied in a given series of experiments.

It would be premature to discuss the results here, but they indicate that much more information is required before the physical chemist is in a position profitably to discuss the mechanism of absorption of direct dyestuffs on cellulose. At the same time industrial experience has shown that there is a very great difference—almost one of kind rather than degree—between the dyeing behaviour of "cuprammonium" and of "viscose" cellulose. This difference constitutes an exception to the generally smooth and correlated increase in the absorption of various substances on passing from "natural" to more "activated" celluloses.

J. Text. Inst., 15, T157, 1924; 19, T77, 1928.
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# THE PHYSICAL SIGNIFICANCE OF CRIMP OR WAVINESS IN THE WOOL FIBRE.

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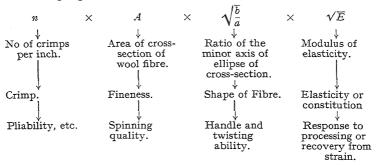
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### The Physical Significance of Crimp or Waviness in the Wool Fibre.

If the wool fibre is considered as an elastic medium to which the ordinary law of bending will apply, it may be shown that the formula due to Euler for the bending of a strut, could be applied by rendering it into the form

$$nA\sqrt{\frac{\bar{b}}{a}}\sqrt{\bar{E}}={\rm constant}.$$

This formula might be expressed diagrammatically according to its manufacturing significance, as follows:—



It has been shown from actual measurement (S. G. Barker and Norris), that the value of the constant expressed above is roughly of the order of  $9 \times 10^{-6}$ .

In a study of the number of crimps per inch as obtained by Duerden for different qualities of South African Merinos, Barker and Norris tested the validity of the formula stated above, and found that Duerden's data shows striking approximation to a curve corresponding to

$$n \cdot d^2 = \text{constant},$$

where d indicates Duerden's fibre diameter measurements.

Another treatment of Duerden's results due to Oliver gave a formula as

$$n \cdot d^{2\cdot 4} = \text{constant}.$$

It is significant, however, that if instead of "diameter," the true area (A) of the ellipse of cross-section be taken, the formula becomes

$$n \cdot A = constant$$

and this is a much closer approximation to the truth.

We thus see that there is a distinct relationship between the number of crimps per inch of the fibre and its fineness, as expressed by its area cross-section. This of course is what one would expect if the fibre is assumed to be an elastic rod. Until comparatively recently, however, the significance of this relationship somewhat masked the real issue as far as the growth and production of the waves were concerned, in that investigatory effort was concentrated upon ascertainment of the number of crimps per inch rather than the total number of crimps per fibre.

In the course of some work in Australia, under range conditions, Lefroy called our attention to an observation made on the growth of individual locks of wool over a period of twelve months. The number of crimps or waves produced in each successive period of four months was apparently constant, *i.e.* on the sheep under investigation, ten crimps were produced in each four-monthly period, but the length of the individual fibres of the wool, as also the thickness along the staple due to drought, etc., was distinctly variable.

It is easy to realise that if these observations can be proved as a general rule, we are led inevitably to the conclusion that crimp forma-

tion is a period function of time, independent of fibre length.

A consideration of the formula initially quoted above indicates that each factor of the mathematical expression intimately concerns some phase of industrial processing, and of these factors crimp or waviness presents an interesting problem both to the Physicist and the Biologist.

In a further consideration of Euler's theory, Callandreau studied the form assumed by a homogeneous rod of constant section when acted upon by a force at one end in the direction of the initial direction of the axis of the rod. He found that, in general, the rod would bend into a wave form which may correspond to a single half-wave, or to a number "n" of half wave lengths. Callandreau's theory is more complete than that of Euler, and takes into account terms previously neglected. It would seem therefore that if an elastic rod acted on by such a force along its length, could assume a crimp form showing a number of undulations, we have roughly got something which is similar, at any rate in form, to crimp or curly wool fibre.

As already mentioned, little significance had previously been attached

to the total number of crimps per fibre along its entire length.

In association with the author, Norris and Van Rensburg investigated the relationship of fibre length to the total number of crimps per fibre in a lock of wool selected haphazard from any part of the fleece, independent of the length of the fibre. Fibre length in the same lock may vary greatly, say 2 or 3 cms., the difference being in some cases as much as 9 cms. between the shortest and the longest fibres, but the average total number of crimps per fibre, however, does not show any corresponding variation. In many locks, the mean total number of crimps in each fibre was the same irrespective of the length of the fibre, whilst in many other cases it was also constant, except for very short fibres, which may be considered as anomalous cases.

It was apparent that in the case of various wools examined, of many breeds and sources of origin, the general rule emerges that crimp formation is a periodic function of time irrespective of the length of fibre produced in that time. As a consequence of this general rule, it is obvious that if the number of waves is to be the same and yet the length of the fibre is to vary, the amplitude of each wave will vary, that of the longer fibre being greater than that of the shorter. The results are represented graphically in the figures.

Since no other factor but the mean total number of crimps is involved in the ordinate, it shows that the straight line parallel to the abscission (fibre length) indicates that the mean total number of crimps per fibre is in no way dependent upon or regulated by fibre length, but remains constant.

In continuation of this work Norris and Claassens studied a set of samples of Merino wool taken from the same fleece by Duerden at intervals of one month during its entire life of thirty-one months. The figures obtained showed clearly that the number of crimps per centimetre of straightened fibre systematically decreased with increase in fibre length. In order to arrive at an approximate idea of the rate crimp formation on this particular Merino fleece, the mean number of crimps per fibre for each monthly sample was plotted against the age of the sample.

From the slope of the best straight line through the points it was estimated that approximately four crimps per month had been produced, and these were produced with striking regularity. The data obtained showed that whereas there was a considerable variation in the length of the fibres within particular locks, as also in the average number of crimps per fibre from the locks, there is apparently no connection whatever between these two variables.

A further paper by Norris recorded similar results from New Zealand wool, and it became obvious that the observations already referred to made by Lefroy were confirmed and clearly indicated the complete independence between the total number of crimps per fibre and the fibre length, and furthermore, since the number of crimps per fibre, produced in the same time, was the same for different fibres in the same lock, the crimp may therefore be regarded as a periodic function of time. It may perhaps be permitted therefore for a physicist engaged in such study to indulge in what may be regarded as a flight of biological imagination as regards the origin of crimp in the follicle.

S. G. Barker and Norris (1930) suggested a complete mathematical analysis of the different forms of crimp. A method of expression due to Tunstall was used, when it was shown that by the assumption of two forces creating simple harmonic motions in directions at right angles to each other in the follicle each and every form of crimp could be explained.

It was pointed out that all types of curl and crimp are found in wool samples, varying from a simple spiral to uniplanar crimp waves. In every form all portions of the fibre in its unstrained state lie within a short distance of the axis of that form.

(I) When the fibre assumes a helical formation we get an approximation to the form obtaining in a spiral spring where the axis of the spring is inclined at a finite angle to the horizontal. A not infrequent occurrence in this type of curl is a reversal in the direction of rotation of the spiral, a right-handed spiral may become left-handed and vice versa.

(2) When the waviness lies in a single plane, the plane may remain constant throughout the length of the fibre or may be found to twist, so that when a fibre is placed on a flat surface the plane of part of the crimp will be in the same plane as that surface, and part will be in a plane or planes inclined at an angle to the plane of that surface.

The following mathematical study, due to Tunstall, is a preliminary

contribution to a geometric study of the fibre form:-

Denoting by z the distance of an element of the fibre form, say, the skin, and x and y the perpendicular co-ordinates of the element in a

plane perpendicular to the fibre, the most general form of a fibre can be represented by the equations

$$\begin{aligned}
 x &= a\theta \\
 y &= b\phi \\
 z &= ct
 \end{aligned}$$

where  $\theta$  and  $\phi$  are oscillatory functions of t, an independent variable, which is intimately related to, or which may be, the time of growth of the fibre; a, b, and c may be regarded as constants over relatively short periods of t, although all of them are probably functions of t also over long periods.

The simplest oscillatory function of t is the sine function, and we shall assume for the detailed consideration of the problem that the

equations

$$x = a \sin \omega t$$
  
 $y = b \sin (\omega t + \alpha)$   
 $z = ct$ 

represent the simple forms of the fibre, each of these simple forms corresponding to appropriate values of a, b, c, and  $\alpha$ .

For example, if a, b, or  $\alpha$  be zero, the form of the fibre so represented will exhibit uniplanar crimp of definite amplitude and wave-length. Alteration in the number of crimps per unit length may then be due to a change in the value of  $\omega$  or of c.

Further, if  $\alpha$  remains zero, while  $\alpha$  and/or b, vary, the plane of bending will alter. It is possible, for example, to account for a rotation of the plane of bending while the amplitude remains constant by simultaneous variation of  $\alpha$  and b, so that the sum of their squares remains constant. The adjoined table shows how the values of  $\alpha$  and b vary, so that the sum of their squares is equal to 100, and the table gives the corresponding rotation of the plane of bending:—

$     \begin{array}{c}       \theta \\       b \\       a     \end{array} $	0° 0	5·7° 1 9·95	11·5° 2 9·80	17·5° 3 9·54	23·6° 4 9·16	30° 5 8·66	36·9° 6 8	44·4° 7 7·14	53·1° 6	64·2° 9 4·36	90°
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This type of change of form has been observed in many cases. Again if a and b remain constant, while a varies, say increases from zero, the uniplanar wave form will change first to a curl, formed as it were on a flat elliptical cylinder until, when a becomes  $\frac{\pi}{2}$ , the cross-section of the moulding cylinder would be an ellipse of axes 2a and 2b.

In the particular case when a equals b, and when  $a=+\frac{\pi}{2}$  the fibre would take the form of a helix of definite radius and pitch, while if the value of a changed to  $-\frac{\pi}{2}$ , the form would still be a helix of the same radius and pitch, but whereas the first would correspond to a right-handed screw, the second would be left-handed.

Two such forms in the same fibre have been observed, and in view of the special interest attached to such an effect, the geometrical theory will be considered in detail. The right-handed screw of radius a and pitch p is represented by the equations

$$x = a \sin \omega t$$

$$y = a \sin \left(\omega t + \frac{\pi}{2}\right) = a \cos \omega t$$

$$z = \frac{\omega}{2\pi} pt$$

and the corresponding left-handed screw by the equations

$$x = a \sin \omega t$$

$$y = a \sin \left(\omega t - \frac{\pi}{2}\right) = a \cos \left(\omega t - \pi\right)$$

$$z = \frac{\omega}{2\pi} pt$$

The change from one screw to the other is usually slow, corresponding to a change of about  $\frac{2\pi}{c}$  in the value of t.

Taking as our zero of t the value corresponding to the onset of the change, the form of the fibre over the change will be represented by

$$x = a \sin \omega t$$

$$y = a \cos (\omega t - \theta)$$

$$z = \frac{\omega}{2\pi} pt$$

where  $\theta$  is the total lag of the y component on the x component introduced during the interval o-t.

Let us now suppose that the lag  $\theta$  is proportional to t, and that the total lag  $\pi$  occurs in time  $\frac{2\pi}{\omega}$ . We then have the following equations to represent the form of the fibre during the change:—

$$x = a \sin \omega t$$
$$y = a \cos \frac{\omega}{2} t$$

the equation for z being dropped, because in observations of the form of the fibres x and y components are of greatest interest. The projection of this form on the x-y plane is given in Fig.

of this form on the x-y plane is given in Fig. . It appears, however, that our assumptions are equivalent to the assumption that there are sudden changes in the period of the y component. As it will obviously be difficult to assign any cause to such an effect, we proceed to consider an alternative suggestion.

We shall now suppose that the phase retardation is due to a continuous uniform change in the period of the y component from its normal value to a new value and back to the normal value. This assumption involves no such discontinuity as that mentioned above.

We now write the equations for the fibre during the change of form—

$$x = a \sin \omega t$$
$$y = a \cos \phi$$

in which  $\frac{\partial \phi}{\partial t} = \omega(\mathbf{I} - Kt)$  so that

$$\phi = \int_0^t \frac{\partial \phi}{\partial t} dt = \omega t \left( \mathbf{I} - \frac{1}{2} K t \right)$$

these equations to apply until  $\frac{\partial \phi}{\partial t}$  reaches its minimum value.

If this minimum value be reached when  $t = \frac{\pi}{\omega}$  and if at this time the

lag introduced be  $\frac{\pi}{2}$  we have

$$K = \frac{\omega}{\pi}$$

so that our equations become-

$$x = a \sin \omega t$$
  
$$y = a \cos \omega t \left( 1 - \frac{\omega}{2\pi} t \right)$$

If now we take  $\frac{2\pi}{\omega}$  as a new unit of time, so that the new time is given by

$$\tau = \frac{t}{\frac{2\pi}{w}}$$

the equations assume the more manageable forms

$$x = a \sin 2\pi\tau$$
  
$$y = a \cos 2\pi\tau (I - \tau)$$

and, for the next half period during which the period of the y component returns to its normal value, we have

$$x = a \sin 2\pi\tau$$
  

$$y = a \cos \{\pi - 2\pi\tau (I - \tau)\}$$

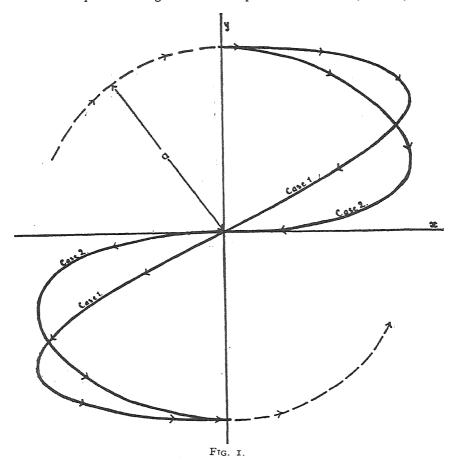
Fig. 1, case 2, shows the form of the fibre during such a change. Several fibres have been observed which show an appearance similar to this.

It appears that appropriate modification of the characteristic equations would bring practically all fibres within this simple scheme, and it remains now to locate the cause of these effects.

There is certainly evidence in the field of biological observation that periodicity or rhythm is not an unusual feature in the growth of hair. Thus the hair of insectivores and rodents, and also of some other forms, is characterised by a discontinuous medulla. Hollow spaces alternate regularly with bridges of solid material. There is a type of pigment distribution in these hairs that is no less strikingly periodic. Granules may be seen at the proximal portion of each air-space. In an albino rabbit, the granules are colourless, but if the hair is grey, these granules are black. Alternating bands of different colours are often seen in hair, and it is noteworthy that the transition from one colour to the next is sharp and definite. Another type of periodicity was observed in the American opossum (Cœnolestes) in which hairs showed a regular alternation of portions with and without medulla.

In the growth of feathers in birds far more striking rhythms are to be found. Apart from such alterations in colour as is shown in the barring of breeds of fowls, such as the Plymouth Rock, there is the case of the ostrich feather in which it has been demonstrated that alternating bands reflect the difference between day and night temperatures.

The essential feature of crimp, however, is the conclusive proof of the existence of periodicity or a regular occurrence of some state along the fibre. Periodicity, both in time and in space, has long been regarded as a characteristic of biological systems, but of recent years a considerable amount of work has been done to show that periodicity is at least as common in ordinary, simple, physico-chemical systems, in many cases consisting entirely of inorganic materials. It may therefore be that periodic biological structures and functions are controlled by the same processes as those operating in the physico-chemical cases. Although it is not possible to go into this aspect in detail here, it may be



said that there is already some evidence to show that both the biological and physico-chemical phenomena are affected similarly by a change of condition.

E. S. Hedges has shown that the formation of the periodic structure is not a result of periodic chemical reaction in certain cases, but it is a secondary phenomenon taking place after the completion of the reaction. He cites instances of periodic actions and periodic structures, distinguishing carefully between the two. As an illustration of periodic structure of crimp form obtained by coagulation Hedges puts forward the following:—

"A I per cent. sol. of arsenious sulphide was contained in a series of capillary tubes, open at one end, which were then immersed in solutions of ferric chloride, varying in concentration from I-30 per cent. In these capillary experiments definite bands of precipitate were not formed, but the coagulum consisted of an undulatory filament, the distance between successive peaks of the waves being generally 2 mms. The experiments were repeated in the laboratories at Torridon by Norris. This is a new kind of artificial periodic structure resembling the crimp of many natural fibres, but a more detailed investigation of this phenomenon has not yet been carried out. It is the nearest approach to the type of periodicity exhibited by the wool fibre.

"The essential position for periodicity appears to be the existence of some critical condition, determining a change which proceeds to completeness once the critical value is reached. In an investigation of the cause of periodic phenomena in electrolysis and in the chemical passivity of iron, it has been shown (Hedges 1929) that these phenomena are determined by the rate at which a certain critical concentration of ions can be reached by diffusion. In the formation of periodic structures by diffusion and precipitation it seems probable that a critical concentration is again involved; at least, the coagulation of sols by electrolytes

is associated with a definite threshold concentration."

A theory of periodic structures as affording a possible explanation of hair growth is mentioned by Copisarow (1931) in a paper on the mechanical fundamentals of periodicity in reactions and structures. After reviewing various natural periodic phenomena he remarks that where colloid reactions take place within the limits of capillaries, the band, ring or stripe structure disappears, i.e. the bands or rings become drawn out along a long thread which, in consequence, exhibits a crimped or wavy The case, already quoted, of the coagulation of arsenious sulphide is cited as a concrete instance. Coparisow remarks that this aspect of the phenomenon is interesting in that it probably exhibits something of the natural process of hair growth. The colloidal embryonic medium in the follicle bulb, passes through the capillary tubes furnished by the canal pores through the epidermis or elasticum. One has to consider the possibility of such conditions influencing the formation of the hair whilst it is still in incomplete filament form, even during formation in the restricted tube, resulting in a fibre product having the usual wavy form of crimp.

Coparisow postulates mechanical assumption as being the fundamentals upon which such periodicity is established, including within its scope all rhythmic formations involving space and time, such as, e.g. periodic reactions of a physico-chemical character, and the formation of periodic structures. The slow flow and coagulation of the fibroin in the formation of silk may be similarly viewed. Thus again we have additional evidence for the physico-chemical explanation of the formation of crimp, and it is obvious that such arguments as are put forward above cannot be lightly disregarded in this connection.

Lloyd and Moravek, in a recent paper on periodic precipitation, give copious illustrations of chemical periodic phenomena. They also dis-

cuss the probability of periodicity in biological reactions.

The chief points of contact between this pure research and the problem of crimp in wool are that wool is a colloidal substance, the fibre has a large specific surface, crimped artificial fibres have been prepared and both uniplanar waves and spiral are known in the artificial as well as in

the natural structure, and fineness of texture goes with increasing degrees of crimp. The conditions of production of the wool fibre are therefore those where the principles of periodic structure may be expected to operate.

We thus have three possible means for explanation of the formation

of crimp:-

(I) A purely physical phenomenon, the result of periodic forces, and

(2) An undulatory structure, the result of periodic physico-chemical reaction, and

(3) The formation of a wavy structure, as explained by Callandreau for elastic rods, simply by a lateral pressure along the length of a semi-plastic fibre.

In the latter case one might refer to the group of curves known as "elasticas," produced by deformation of elastic rods of uniform cross-section when forces are applied at their ends, along their length to which, in point of shape, the different types of crimp conform with great similarity. If crimp really has an origin similar to that which accounts for the formation of "elasticas" then it would seem that the force producing this deformation, which results in crimp, must operate within the follicle. Further, the extruded portion of a fibre would not contribute in any way to the crimpiness exhibited, otherwise the wave form would alter in a progressive manner with the growth of the fleece.

Evidence of compression within the follicle is furnished by examination of the fibres in polarised light. In a note on the optical activity of natural silk, Ongaro (1931) found that the optical activity was due, not to molecular or crystalline rotatory power, but to a phenomenon of birefraction, the accidental nature of which is revealed by the variability in the orientation of the extinction of different fibres. The fact that the optical axis of the fibre is in the direction of the latter is regarded as evidence that the silk is subjected to pressure during its emission. Preston, in his paper on a "Skin Effect on Viscose Rayon," notes the same type of phenomena in the production of rayon, and concludes that during the spinning of the filament there are two orienting influences bearing on the arrangement of the micelles, namely, the hydrodynamical friction due to extrusion at the jet orifice and the "draft" to which the filament is subjected. In the case of wool, the progress of extrusion is slow, and as shown by Wildman, the fibre is probably fully keratinised before this occurs, hence the former influence is probably absent, but the pressure, periodic or alternating, inside the follicle creating periods of compression and rarefaction may be present. In a privately communicated note on the subject, Preston remarked: "the variation in the orientation of the extinction of different fibres, referred to by Ongaro, probably means the local and microscopic variations such as are seen in one of the microphotographs of wool I have sent" (see Fig.

). There seems, therefore, to be direct evidence of variations of pressure during formation or extrusion of the wool fibre, and this line of enquiry may yield very interesting information on follicle mechanism and fibre growth.

However, it is significant that for purposes of analogy and mathematical treatment, the Euler and Callandreau expressions can be made significant as regards the interpretation of the inter-relationship of the different attributes of the fibre. If, on the other hand, the theory involving two simple harmonic motions is tenable, then we have to locate proper forces of such periodic character.

Recent work by Wildman in the Zoological Department, University of Leeds, on the growth of hair in the follicle, has shown that there is a suggestion of the possibility of a periodic rotation of the follicle bulb within the skin.

Before discussing the matter further let us take cognisance of the external evidence available with regard to the possibility of the follicle rotation.

Davenport and Ritzman, in their paper on "Wool Characters and their Inheritance," made the following statement:—

"In intermediate and mixed breeds the wool fibre forms a spiral of

one millimetre or greater diameter."

Then, again, in his treatise on hair, Danforth quotes instances of similar observations. In discussing the possibility of a twist in human hair he stated that:—

"Generally the twisting consists of a series of half turns so that one side of the hair is alternately toward the observer and away from him. The length of hair that is involved in the twist ranges from less than a millimeter to several millimetres, or so great a distance that it is difficult to detect any twist at all. In general, the twisting is not continuous but interrupted. When the twists or half turns involve only a short distance on the hair-shaft, and especially when two or more twists occur closely together, the hair tends to change its direction in a way that gives it a peculiar frizzy character. Since this apparently irreversible twisting of the hair on its own axis may be seen even within the follicle, there is some probability that it is determined there, perhaps by irregular or periodic changes in the function of the papilla, or by irregular compression of the sheath immediately above. Strangely, this characteristic has been as much neglected in hair work as some of the other traits have been emphasised. It deserves more careful study, and may be found to have a greater anthropologic significance than a cross-sectional form."

Burgess, as recorded by S. G. Barker and Norris, discovered a similar twist in the fibre of the Russian sable, which was otherwise supposed

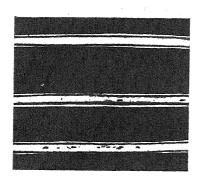
to be perfectly straight.

Still more recently, Rossouw, of South Africa, working in the Wool Industries Research Association's laboratories, in an examination of the phenomenon of crimp and the relationship of the plane of bend to the major axis of the fibre, discovered that the uniplanar crimp of the merino could not be considered except as having, not only the undulations of the ordinary crimp, by at the same time a twist of the fibres within the waves. In each case it was found that a reversal of the angular rotation of the plane of the minor axis, which oscillated through approximately 180°, corresponded with a crest or trough of a crimp wave.

It is interesting to note that in Rossouw's work it was found that in order to define this path at all accurately it was necessary to measure the fibre at very close intervals along its length (0.005 cm. to 0.040 cm.

depending on the thickness of the fibre).

A significant point in Rossouw's findings is that the period of the fibre twist corresponds exactly to that of the wave form, that is, the approximate position of the crests and troughs coincides with the points of reversal of the direction of twist in the fibre. Danforth noted a similar occurrence in human hair. Fig. 2 illustrates the case perfectly. The natural fibre was found to have a gradual twist increasing to 180°, and after this a reversal of twist proceeding to 180° in the opposite direction, or in other words a progressive rotation. The length of the fibre re-



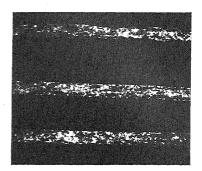
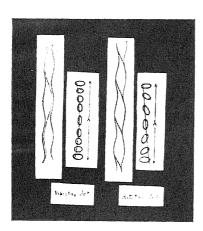


Fig. 2.

Magn. × 65.

Fig. 3.



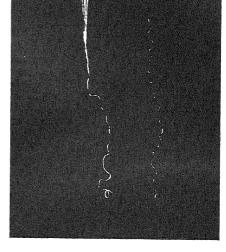


Fig. 4.

Fig. 5.

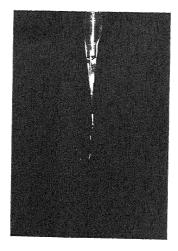


Fig. 6.



presented in Fig. 3 corresponds to one crimp wave. It will be noticed that the reversal of the direction of twist coincides with the trough of the wave in this case, and further measurements along the fibre show the necessary reversal coinciding with the crest of the wave following.

It is, therefore, established that the wool fibre in these particular cases exhibits two phenomena, namely, the undulatory waviness called the "crimp" and secondly, a twist in the fibre along its length which may be styled "curl."

An interesting point with regard to the differentiation between these two has been brought out by Rossouw in examination of a New Zealand Romney fibre.

Although the crimp appeared to be uniplanar, a close examination showed it to lie along a well-defined, narrow, longitudinal strip, the surface of a cylinder of about 3 cms. in diameter. Although, however, the general shape of the crimp appeared thus to be a cylindrical strip parallel to the axis of the cylinder, in the actual detail it was much more complicated. Thus, examining the fibre from root to tip as it lies on the concave surface of the cylinder, the wave appears to be of the following shape. Starting from the axis of the crimp wave up to the crest it lies on the cylindrical surface, here it lifts out into the cylinder and gradually meets the surface again about half-way towards the axis, remaining in the surface until it reaches the turning-point in the trough. It is then bent slightly into the cylinder as at the crest, meeting the surface again about half-way towards the axis.

This finding agrees very well with one of the diagrammatic representations (about 300 diameters) of crimped wool fibre as detected by W. von Nathusius (1866). From the diagram, however, it appears that he did not observe any rotation of the axes of the cross-sectional ellipse.

Hirst and King (1926) noted similar rotations in the case of mohair and wool fibres examined by them. Measurements along the fibre showed a definite undulation, the major axis alternating from one direction to that at right angles to it. This suggested a cylindrical rubber rod distorted by applying torque at one end. The effect was specially observable with merino fibres, but was practically absent with coarse Lincoln fibres. The correspondence between crest and trough of the wave form, and the position of rotation of the major axis of the fibre, was noted.

From the work of Wildman it would seem natural to attribute the fibre twist to a possible rotation of the bulb of the follicle. There is evidence, however, with regard to the wave form that the crimpy nature of the fibre actually assumes its shape before protrusion from the skin. Further, during the period of formation or growth, the fibre root-sheath cannot be regarded as a mould but must be considered as being also in the process of formation, capable of being acted upon by the same forces and influences as the fibre itself, in fact, being a cognate structure with the filament under formation. Hence, any deformation or crimpiness which the embryonic fibre might assume could also be assumed by the root-sheath. These two would then grow out together, the fibre to persist, the root sheath to fall away.

Evidence of the inherent latent ability of the follicle to produce wavy or straight hair is furnished by Russ in a letter to *Nature*, June 13th, 1931. He records how a black rat was exposed over two small areas on the back to X-rays generated in the region of about 150 kilovolts.

To quote his statement:—

"Some weeks after the dose has been given, the hair fell out and the new hair which grew was devoid of pigment and considerably altered in texture, the normal straight hair of the animal being changed to a rather thinner fibre which appeared slightly curly. This result must, of course, be attributed to some action of the radiation upon the hair follicles, and the curliness of hair which regrows, once the surface has been epilated, is a not uncommon observation in children, where epilation of all the hair of the head has been purposely brought about."

It is obvious that follicles which produce apparently straight hair can be caused to produce a wavy fibre by the application of a suitable stimulus. A repetition of these experiments, however, did not produce a crimp except at the tip, *i.e.* in the initial stage of regrowth.

It is probable that if the original hair had been examined a slightly

twisted nature would have been noted.

In the second place, it is also to be observed that the greater waviness was created on a thinner fibre, a fact which is in accordance with other observations on wool.

Just as in the determination of the path of a projectile, the initial angle of the trajectory is one of the governing factors for the determination of the horizontal range of the path, as well as the greatest height that the path will attain vertically, so the angle of the crimp determines the length of the wave horizontally as also its vertical amplitude. It is obvious that the periodic forces and pressures acting within the follicle could supply us with the mechanism for all types of crimp production, and it is therefore of great interest to study the consequences of such forces, namely, amplitude, wave-length, periodicity, etc., more intimately. Such an analysis can be accomplished by a simple technique. Crimped fibres, or locks of small dimensions, are placed between two pieces of glass (cleaned photographic plates) held together by means of rubber bands. These are placed in the slide of an enlarging camera and the magnified image projected on to a screen. It is simple photography to record the imprint of this enlarged image on to a piece of photographic The fibre then appears white on a dead black background. needle or sharp knife is utilised to cut out a stencil of the crimped waves, the line of incision following exactly the lines of the crimp. The paper has now a serrated edge corresponding to the waves of the fibre, and can be installed in a plate carrier of a Grating Periodograph, designed by Foster. The periods of the vibrations and the other factors can then be intimately examined. The German workers on crimp have classified the wave forms under such headings as "flat waves," "highly bent," etc., but no work of the character outlined above has previously been attempted, and certainly the practical relationships of crimp have not been studied previously from this point of view.

More recently, E. Hill, of the Wool Industries Research Association, has suggested possible causes of crimp as seen from the point of view of the colloidal chemist. He has conducted experiments upon the production of crimp in artificially produced protein fibres and appended herewith are his notes thereon.

Since writing this paper, additional evidence has been published by Otto L. Mohr, in the *Journal of Heredity*, September, 1932. Mohr shows that even in white people curly hair is a dominant mutant character in man. A further paper by Tomkinson, in the *British Medical Journal*, December 3rd, 1932, gives illustrations showing the hair in the follicle, having three distinct nodes or twists before its emergence.

## A DISCUSSION OF SURFACE TENSION AND DEHYDRATION AS CONTRIBUTORY AGENCIES FOR THE PRODUCTION OF CRIMP.

#### By E. HILL.

A study of a longitudinal section of the merino wool fibre in situ shows that the hair shaft extends downwards into the follicle in the skin, terminating in a bulb. In the hair bulb the cells multiply rapidly, and as the growth increases the protoplasmic cells on reaching the narrow portion of the follicle appear elongated and become keratinised to form the cortex of the fibre, which in the case of non-kempy wool is solid. The following forces appear to be at work in the follicle: (a) A force resulting from the growth of the hair cells pushing the fibre upwards, and (b) Lateral forces impressed upon the fibre by the follicle walls and its growing lining of epithelium. The reduction in bore of the follicle towards the neck, indicates a corresponding consolidation, or contraction in volume of the soft protoplasmic hair-forming cells.

The resulting wool fibre consists of a solid cortex of keratin surrounded by a layer of epithelium cells, which differ chemically from the cortex. These epithelium cells appear to be stepped, or overlapping, a state of affairs which is created possibly by the extruding pressure of the hair cortex against the lateral epithelium cells of the follicle, modified by the keratinisation process, and forming the serrations of the wool fibre or scales. If we examine the shape of transverse sections of wool fibres, they are generally of elliptical contour, with varying degrees of ellipticity

and irregularity.

If we regard the newly keratinised wool fibre as a plastic hydrated gel, which as it leaves the follicle may be acted upon by the force due to its own surface tension, the amount of the surface tension effect will depend upon the degree of plasticity of the gel and the dimensions of the fibre, *i.e.* the finer the fibre the greater the effect of surface tension relative to its constitution. It may further be acted upon by forces set up due to contraction of the fibre during a drying process, as also by such factors as may be consequent upon its increase in length during growth. Let us discuss these points separately in greater detail.

#### (I) Surface Tension.

If we consider the effect of surface tension on an oval jet, such a steady force will act in a manner tending to reduce the oval contour to a circle and act at right angles to the jet leaving the orifice.

An oval capillary orifice when used for the production of a vibrating jet affords a classical dynamic method of determining surface tension. Adam 1 states, "if a jet issues from an orifice which is not circular, the surface tension commences to rectify the departure from a circular section in the jet, and the momentum of the liquid causes the jet to become unsymmetrical again after passing through a circular form. Nodes and swellings appear periodically on the jet when seen from one side, and from their distance apart the surface tension may be calculated." This statement may be correct for absolutely perfect conditions, but if one considers a liquid oval surface, then when the major axis is vertical, the oval will be in a position of unstable equilibrium. The slightest displacement will alter the centre of gravity, and the force of gravity

<sup>&</sup>lt;sup>1</sup> Physics and Chemistry of Surfaces, Oxford Univ. Press, p. 322.

will then produce an uncompensated torque. The resultant of this torque with the outflowing motion of the jet will produce a twist, and a twisting oval jet will be formed. In the relevant literature, Lord Rayleigh, indicates the difficulty of observing the form of the vibratory jet.

N. Bohr <sup>8</sup> evolved a formula wherein discharge per second, density, velocity of jet, and mean radius of jet are related, which refers to a jet of circular cross-section. He fixed his observation telescope at an angle to the jet which would be the position necessary if the jet consisted of an elliptical twist. In the present work, apparatus similar to that employed by Bohr was set up. The head of water was constant, the rate of flow could be varied by means of a bunsen valve, and the oval glass capillary tube was fixed in a horizontal position in such a manner that it could be rotated. Each glass capillary was marked with two parallel lines on each side of the narrow portion of the tube, so as to indicate at a glance the position of the minor and major axes. A lens fitted with a pair of indicating needles opposite to each other was fixed in a stand convenient for observing the water jet.

On gently unscrewing the bunsen valve, the water was seen to escape from the oval tube in the form of a circular jet without oscillations. On further unscrewing the valve, the so-called oscillations appeared, which were of maximum length along the jet when the valve was removed so that the full force of water could act. The exact form of the jet was difficult to observe, so the lens was then focussed upon a node of the jet, and the needles were set so that the two points on each side were exactly opposite the summits of a node, there being an anti-node on each side. On rotating the capillary tube and at the same time observing the jet through the lens, it was seen that when the capillary tube was turned

through a circular measure  $\frac{\pi}{2}$  radians, the two needle points were no

longer opposite to the summits of a node, but were now pointing to the middle portion of an anti-node. At  $\pi$  radians the needles now indicated a node as in the first case. Several oval capillary tubes were examined and the same phenomena were observed. The results indicated that the jet was either (I) oscillating from an oval section (the node) through a circular section to an oval section at right angles (the anti-node) and then through a round section back again to the oval section in the same plane (the node) forming a wave-length, or (2) merely twisting, in which case all sections would be oval, and it would twist from an oval (the node) round to an oval at right angles (the anti-node) back again to an oval in the same plane (the node) forming a wave-length.

It was decided to increase the size of the jet to obtain if possible a better production and view of the so-called vibration. Portions of the end of the conical oval capillary tube were cut off and discarded, and the larger oval nozzle end thus produced was carefully filed flat at right angles to the tube, polished and cleaned. On replacing the tube in the apparatus, and viewing jets successively increasing in size, finally a jet of water was obtained which was twisting and not truly oscillating. From an end-on observation of the nozzle, the rotation of the jet was seen to be in a clockwise direction. The cross-sections of the capillary

<sup>Lord Rayleigh, Proc. Roy. Soc., 29, 81, 1879.
Prof. N. Bohr, Phil. Trans., 200A, 281, 1909; Proc. Roy. Soc., 84, 395, 1911
Freundlich, Colloid and Capillary Chemistry (English translation, p. 13).
Barker and Norris, J. Text. Inst., 21, 19, 1930.</sup> 

tubes appeared from inspection to be fairly true ovals. The form of the jet due to surface tension effects was thus observed, but no surface tension determinations were made.

By the use of an ordinary oval capillary tube a rotating jet was thus produced, and since wool fibres in cross-section are of varying degrees of ellipticity, the force of surface tension on growing wool has to be considered as a possible cause of crimp. The degree to which its influence will be felt will depend on the degree of firmness of the gel, and also upon the cross-sectional area of the elliptical extruding wool fibre as it leaves the keratinisation zone. The force of surface tension possibly exerts a very small effect in influencing the formation of a twisting curl in the growing oval wool fibre, but nevertheless must be considered in this connection.

### (2) Dehydration.

Forces due to the dehydration of the gel of the steady growing wool fibre while it is leaving the follicle may now be discussed, and two sets of forces must be considered, namely: (I) the forces of contraction acting on the cross-sectional area of the wool fibre, and (2) those forces acting along its length, their mutual influence depending on the characteristics of the gel. The contraction along the different axes of the cross-sectional ellipse will vary according to the regularity of the contour, size of crosssection of the fibre, rigidity of the gel, moisture, or other volatile substance content which dries out. The resultant of any uneven forces thus set up with those of the contraction along the length of the fibre will tend to cause a twist or curl, thus affording another potential contributory factor, acting towards the formation of a twisting curl in the growing fibre. The principal contraction of the growing wool fibre, due to the dehydration of the gel, will create effects along the length of the fibre. A consideration of the force along the wool fibre created by the drying whilst it is fixed at one end and free to move according to the forces impressed, may be attributed as the cause of the natural wavy crimp of wool, since we have the necessary conditions for the case of an elastic rod, fixed at one end with a force acting along its length. The curve of the crimp can thus be explained as the results of compressive force of dehydration, acting possibly according to Euler's formula, or Callandreau's extension thereof, along the length of the fibre. crimp will therefore depend upon the degree of loss of the moisture or volatile content, the size and form of the cross-sectional area and the rigidity of the gel.

Under these circumstances, if crimp and curl in wool are produced by the simple normal steady extrusion of the growing fibre from the follicle, under the influences of forces such as are outlined above, it should be possible to reproduce the main of these effects experimentally.

In order to get as near as possible to the natural phenomena some artificial fibres were made by extrusion from simple jets, the fibre material being composed of an irreversible protein gel which would possibly behave like wool.

After preliminary experiments albumen from fresh eggs was used as being a suitable and convenient protein. A set of oval glass capillary tubes were made, each in the form of a medicine dropper with a very soft rubber bulb fixed at the non-capillary end. A tube was filled with egg albumen and the tip of the capillary was dipped below the surface of dehydrated alcohol in a tall narrow beaker, and by means of pressure

on the soft bulb an oval jet or filament of albumen was squeezed out. When the jet reached the bottom of the beaker the flow was stopped, and the tube was kept perfectly stationary in the alcohol until the oval fibre of albumen had coagulated. The tube with adhering albumen fibre was carefully lifted out of the alcohol, and the bead of albumen at the bottom of the fibre clipped off with a sharp pair of scissors. The albumen fibre quickly commenced to dry, and during this process the fibre was seen to go into crimps longitudinally similar in appearance to those of wool whilst at the same time it also twisted or curled.

Several fibres were made, and the photograph below (Fig. 5) shows a fibre attached to the jet and alongside is a wool fibre for comparison.

It was noticed that the longer artificial fibres possessed more extended crimps than those of the shorter fibres, similar in fact to those obtained naturally in long wool. This was thought to be due to some effect related to the length of the fibre. A long fibre was made, and when drawn out of the alcohol was cut off short to produce a short filament attached to the tube. This short fibre on drying gave a curl and crimp of larger amplitude and shorter wave-length corresponding closely in form to the curl associated with short lamb's wool. The following photograph (Fig. 6) illustrates an example of such a short fibre.

In view of the above experiments, although it may be argued that a growing fibre takes a very considerable time to be formed, whereas the above are formed in a few minutes, the same set of forces may, however, be supposed to operate in both cases during the dehydration period.

#### "Other Factors Affecting Crimp" (S. G. Barker).

One other point should be mentioned with reference to crimp. Recent work by Burgess in our laboratories and by Gabriel in New Zealand, has shown that the cortical cells can be separated from wool by a process of bacterial retting. Gabriel indicated that where crimped wool was treated, the cortical cells themselves appeared to possess a distinct curve, and in an examination of Lincoln, Romney and Merino, he obtained results which may be set out in Table I:—

Crimp of Fibre. Wool General Appearance. Curvature of Cells. Approx. Radius of Curvature. cms. Frequent broad cells and Lincoln Straight I.25 to 2.5 split cells. Romney Few broad cells Many slightly curved ·3 to ·5 Ends often taper to long Merino Most cells distinctly curved .07 to .15 fine needle points

TABLE I.

Burgess has tested a number of wools of various degrees of crimp and taking the numbers per thousand fibres, he obtained the results in Table II.

Under these circumstances, it is evident that where crimp is a feature of the fibre, then the cortical cells take on a distinct curve. This point is of manufacturing significance.

It would seem therefore that the origin of waviness in wools may be

TABLE II.—One Thousand Readings Selected at Random from Five Different Portions of Material.

		Shape of Cortical Cells.			
No.	Sample.	Straight.	Slightly Curved. (A Feature Related to Crimp.)		
1 2 3 4 5 6 7 8	Rabbit Wool (ordinary)	 802 893 923 924 606 991 930 961	190 104 68 73 393 66 12		

attributed to various causes as outlined above, and each one of these needs careful investigation in conjunction with the biologist.

Crimp may therefore be caused by:-

- (a) Dehydration of the gel with consequent application of a force along the length of the fibre, similar to that put forward by Callandreau.
- $(\bar{b})$  Physico-chemical forces at work in the follicle during the formation of the fibre itself.
  - (c) Surface tension effects, although this is unlikely.
  - (d) Rotation of the bulb of the follicle as indicated by Wildman. (e) A combination of all these.
- The evidence before us would indicate that provided two simple harmonic forces acting at right angles were provided, then all forms of crimp could be obtained. It is a matter therefore for the colloidal investigator, together with a histologist, to go further into the question of what happens in the follicle itself, or, in other words, what is the real process of the reaction which causes the formation of the hair as a chemical and physical entity.

The dehydration theory receives support from observations made by D. Jordan-Lloyd that "the embryonic tissues are the most active of all and may under certain conditions contain as much as 95 per cent. of water". She further points out that "the biochemically active tissues of the adult contain about 80 per cent. of water, with the exception of certain tissues, such as the skin which contains only a comparatively small proportion of biochemically active cells and a larger proportion of biochemically inactive structures, namely the fibres." From this and other evidence the presence of a large proportion of water in the primary protoplasm of fibre material may be assumed, so that the formation into the more solid structure would be accompanied by dehydration.

#### Colloidal Theories of Crimp Formation.

Hill has observed that wool may be considered as a "gel." Hedges, in his book in "Liesegang rings" makes the following remark on "gel" structure in explanation thereof: "According to another view, the particles arrange themselves into fibres or hairs which are intertwined, giving a structure like a heap of horse hair. Such an arrangement accounts for elasticity and the ready diffusion of salts, and in some cases there is direct evidence of the existence of such fibres."

That Hill's suggestion is possible and reasonable is borne out by the many gel characteristics of the wool fibre. Hedges and Henley have described the formation of periodic structure by the coagulation of a colloidal solution containing a gel, and cite as example experiments performed with arsenious sulphide sol and ferric chloride or aluminium sulphate at various specific concentrations. These experiments led to others performed on the coagulation of colloidal arsenious sulphide by ferric chloride solutions in the absence of a gel, using capillary tubes as containers for the arsenious sulphide. These experiments were also repeated by S. G. Barker and Norris, and crimped filament-like structures were obtained.

In discussing a general theory of such periodic structures, Hedges remarks that just as in physiology "according to which a system does not respond to a stimulus until this reaches a threshold value; after which the response is complete when that value is reached," periodic reactions and periodic structures can be linked together therefore, if it can be shown that a critical condition is an essential factor in the formation of periodic structure. Hedges points out that all the principal theories of periodic phenomena involve a critical condition, e.g. those of Wilhelm Ostwald, Bradford, Wo. Ostwald, Dhar and Chatterji, etc. Hedges points out that the critical condition may assume a variety of forms. "The critical condition" may be a certain degree of supersaturation (Wi. Ostwald and Bradford) or the critical concentration of electrolyte required for coagulation (Dhar and Chatterji) or a critical state of chemical equilibrium (Wo. Ostwald).

The possibilities do not stop there and other critical conditions, such as e.g. the super-cooling of melts may constitute one of the factors in the formation of certain periodic structures. The other factor concerned is the "mobilisation of the material" which may be ascribed to diffusion or adsorption or both. For the creation of periodic structures the mobilisation of the material must occur during the delay caused by the "critical condition" being attained. In periodic structures produced by coagulation, it may be argued that the sol is not mobile. On this point Hedges remarks that "periodic structures will not be formed if the sol is completely immobile, but generally the sol will be poly-disperse, containing particles of all degrees of mobility. Moreover, the presence of a peptising agent may keep a portion of the sol in a highly disperse, mobile condition."

"It would seem, therefore, that coagulation is the principal process in the class of structures recognised by Dhar and Chatterji, where a layer of precipitate is followed by a layer of peptised sol; these structures indicate that a certain portion of the sol formed under these conditions is mobile and accumulates in the rings and the rest is immobile and remains in the spaces." In Hedges and Henley's experiments on the periodic coagulation of colloidal arsenious sulphide it was observed that the rings did not contain a great deal more substance than the intervening spaces, again showing that only a portion was mobile. Hedges remarks: "Where the sol contains a very small mobile fraction, definite bands and spaces cannot be expected, but a slight thickening may occur periodically," and this would explain the formation of the crimped coagulation fibres and filaments previously mentioned. On the other hand, in view of Hill's theory of dehydration or drying of the gel as a cause of crimp, one would observe that according to the work of Bary and others, "' pectographs" have been prepared from various colloidal solutions

which exhibit periodicity. Bary's work shows that, in general, hydrophilic colloids give a continuous deposit on drying. Pectographs obtained from colloidal ferric hydroxide hydrosols consisted of a series of

parallel filaments or lines of deposit.

Microscopic examination of the filaments revealed numerous fibrils arranged parallel to each other with their long axes in the direction of the filament. The fibrils are held together by a reddish brown material or cement. Similar pectographs are obtained from colloidal solutions of chromic and aluminium hydroxides. The former has less fibrillar constituent and the latter is rich in the interfibrillar cement. Burgess, Waters and others has shown wool to consist of cortical cells or fibrillæ parallel to the length of the fibre held in position by means of a cement-like material which can be retted out by suitable bacterial organisms. Bary explains the pectograph phenomenon on the ground of provision of the critical condition by the free electrolyte in the colloidal solution, which by evaporation in the surface reaches a concentration at which it coagulates the colloid, thus forming a band of deposit. Periodic capillary structures may also be formed, and Schultze describes periodic structures formed in capillaries through evaporation. Thus the dehydration theory of Hill may also be a valid explanation even taking into account the possibility of the formation of periodic capillary phenomena. The question may be raised as to why different degrees of waviness or crimp are found in various animal hairs or even in animals of the same species. The possibility of follicles occurring in which the critical condition does not arise would seem a plausible reason.

It is quite possible for a reaction to proceed to its final state without periodic phenomena occurring, just as also, in the course of its formation, the critical condition may be reached and periodic formation ensue.

Hedges remarks tersely on the relationship between biological and physico-chemical structures. "A physico-chemical interpretation of the process of living organisms does not necessarily invalidate a biotic energy which causes these processes to occur. At times the life-causes and the physico-chemical expression of the results of these causes become confused, and it is mainly then that scepticism arises as to the value of

physico-chemical interpretations of biological phenomena."

If the dehydration theory be accepted, or whether a theory of critical condition arrived at by gradual evolution of the reaction producing the keratinisation of the primary material of the wool is valid, it is certain that the production of the essential critical condition can receive an external stimulus from sources outside the follicle. The phenomenon of curly hair growing after depilation by X-ray irradiation or after severe illness, where non-curly fibres were previously produced, is evidence that the same follicle can produce either straight or curly filaments according to conditions of production. Until more is known of the actual happenings within the follicle the question will be difficult to answer, but the origin is probably biophysico-chemical in nature, and research on these lines will prove well worth while.

Thus, whilst preserving an open mind on the subject of the causation of crimp or waviness in wool and hair, yet any biological observation or theory which ignores or fails to take full cognisance of physico-chemical colloidal explanations, may possibly be ignoring a very important factor.

## CHEMICAL CONSIDERATIONS IN RELATION TO THE STUDY OF MAMMALIAN HAIR GROWTH.

### PART I. THE SULPHUR ECONOMY OF ANIMAL FIBRE PRODUCTION.

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In the case of artificial fibres, pure research on synthetic processes, and technical enterprise directed to the achievement of a satisfactory efficiency in both yield and quality of product, are indispensable preliminaries to their successful textile development.

The study of scientific principles governing the metabolic processes of natural fibre production, while not correspondingly essential, occupies the same foreground in the sequence of textile development, and is in this sense equally necessary of pursuit before the commercial utilisation of such fibres can be regarded as completely on a scientific basis.

The counterpart to the synthetic fibre-producing unit in the case of wool fibres, with which this paper is more especially concerned, is the follicle itself. The considerations regarding improvement of its product in quality and yield, however, are at first sight far removed from those of the pure and applied research developments, governed directly by physical and chemical principles, which control synthetic fibre production.

Such scientific assistance as has been given in the past to the producer in improving fleece character, has been mainly from the study of nutritional and genetic influences, particularly the former, in their more general effects upon the whole animal, within the limits suited to the locality.

The wool itself did not, as an end product of animal metabolism, interest the biochemist as do the chemical constituents of, and their changes in, living tissues, and was regarded less as of bio-chemical significance than as an amino acid complex offering the organic chemist a knotty problem in chemical constitution.

The study of the principles underlying the follicle mechanism producing it attracted no attention from the chemical side, and remained in the hands of the histologist.

The agricultural and nutritional sciences in indicating conditions for soil improvement, and consequent enrichment of pasturages, and greater freedom from pathological conditions, have contributed in a general way to an understanding of the problem, the gain in well-being of the animal being incidentally accompanied by improved condition of the fleece.

Recently, however, the nutritional aspect has become more definitely focussed upon the fleece production itself, and there has been a growing acceptance of the view that nutritional as distinct from genetic factors can definitely influence, within limits, the nature of the wool supply. Indeed, from the chemist's standpoint it is now not altogether fantastic to regard the follicle as a continuous synthesising apparatus generating

a product whose quality and yield vary with varying concentrations of intermediates charged to it from the blood stream. We are thus approaching physico-chemical principles allied, though far less direct, to those actually governing synthetic fibre production.

Until, however, some measure of chemical comparison of different wools was made available, no insight could be obtained into this aspect

of the problem.

The task of establishing characteristic differences in general composition between wool types is of course even more difficult than between wool and the other animal fibres and integumentary structures designated as of scleroprotein composition, all of which proteins are distinguished by the considerable percentage of sulphur they contain. This, as is well known, serves as a convenient qualitative test, but the variable values for sulphur content recorded from time to time could not be regarded as pointing to any significant difference either in biological origin or chemical constitution.

Prior to the systematic investigations of Barritt and King 1 there was no disposition to regard its presence as of particular significance, or any possible variation from one wool to another as of structural import.

The proof of variable sulphur content in wool (see examples quoted in Table I.), and the substantially sulphur-free nature ascribed to the medulla, which has now been established beyond reasonable doubt 2, 3 afforded the first evidence calling attention to the fundamental chemical importance of sulphur in wool growth.4 The fact that this sulphur is accounted for in its practical entirety as cystine 5, 6, the only sulphurcontaining acid in the group of amino acids recognised as "essential" in animal metabolism, focussed attention on the quantitative aspect of this particular form of sulphur in nutrition which will be discussed later. Arguments, now no longer tenable, were in fact advanced to show that as a biosynthetic protein product the keratin of wool would be expected to have a constant amino-acid composition and therefore a constant percentage of cystine, so that the latter must be a direct measure of the weight of wool produced.

In non-medullated wools the variation, while showing varying incorporation of sulphur into the fibre as a whole, leaves the precise location of this variation in doubt, i.e. whether due to different proportion as between cuticle and cortex, both in their relative masses and their sulphur contents, or to varying composition from the central to the outer cortical cell layers.

An attempt to obtain conclusive proof as to any difference between cuticle and cortex by analysis of mechanically separated scale is in The observation from analyses of complete and descaled human hair 7 that the cuticle and cortex are identical in sulphur content, is scarcely conclusive since the cuticle layer being only one cell thick its removal would have negligible effect unless it were of considerably higher sulphur content. Arguing, moreover, from the theory of the cystine gradient in follicle activity advanced in the succeeding paper, the cuticle cells might be expected to show the highest sulphur content and the

<sup>&</sup>lt;sup>1</sup> Barritt and King, J. Text. Inst., 17, 386T, 1926; 20, 151T, 1929.

<sup>2</sup> Barritt and King, Biochem. J., 25, 1075, 1931.

<sup>3</sup> Bekker and King, Biochem. J., 25, 1077, 1931.

<sup>4</sup> King, J. Text. Inst., 18, 364T, 1927; Text. Merc., 24th Oct., p. 17, 1929.

<sup>5</sup> Marston, Commonwealth of Australia Coun. Sci. and Ind. Res. Bull., 38, 1928.

<sup>6</sup> Epinipaton, Biochem. L. 221, 1929.

<sup>Rimington, Biochem. J., 23, 41, 1929.
Chamberlain, J. Text. Inst., 23, 13T, 1932.</sup> 

cells forming the cortex to show progressive diminution in sulphur con-

tent with their distance from the cuticle layer.

One apparently specific constitutional difference, amongst possibly yet others, between cuticle and cortex—the absence of tyrosine in the cuticle—further complicates the difficulty of deducing any definite chemical constitution from wool fibre as a whole. Acceptance of the gradient theory would in fact preclude the possibility of regarding even its component cells individually as exhibiting any stoichiometric relation of cystine to its amino-acid complement.

It may be pointed out at this stage that wool and hair are the products of distinctive activities corresponding entirely with the subsequent development of the ecto-dermal tissue of the embryo, in which no structures of meso- or endo-dermal origin are involved. The products of ecto-dermal origin may be sub-divided into unorganised, e.g. the skin epithelium, as distinct from organised, like the hair from its follicle.

The integumenta can be considered, for the present purpose, according

to the initial stimulus to their development, e.g.:

 Reptilian scales which involve dermal protrusions pushing out but not breaking through the epidermal layer. This latter is moulted, giving the shed snake-skin.

(2) Feathers, which develop as an epidermal superstructure around a dermal protrusion which is entirely retracted when the feather

growth is complete.

(3) Wool and hair, which arise from an epidermal depression and involve only organised epidermal tissue.

These characteristic differences in development should be reflected in chemical differences in the products.

Obviously the main characteristic of the wool follicle mechanism is its function of absorbing cystine (or cystine complexes) from the blood stream in the dermal region, in which it is deeply seated, but from which it is de-limited, if not by an actual membrane, at least by a definite basal layer of epidermal cells continuous with the basal layer of the

epidermis and forming the contour of the papilla.

The unorganised epidermal development is equally presented with this cystine supply, but apparently utilises it only in much smaller degree. In this connection the view previously advanced that the medulla is simply a direct upward proliferation of the cells of the basal epidermal layer from the apex of the papilla appears no longer tenable in view of the evidence detailed in the succeeding paper. The medulla is evidentally not identical with the unorganised basal epidermal tissue, for the formation of which a cystine supply is adequately available yet only lightly drawn upon, but an alternative product formed owing to non-availability of a cystine supply to transfuse the epidermal boundary of the papilla in the apex region.

The feather development, though again entirely epidermal, differs in what seems a very important respect. In rough analogy with the wool fibre, the periderm, shed in the preening stage, is equivalent to the inner root sheath, the rachis (shaft) casing and its quill extension, to the cuticle, while the packing material or pith within the rachis corresponds to the cortex. This interior, however, is developed in immediate contact with the extensive dermal plug, almost filling the quill in its early stages with copious blood circulation within it. The epidermal "cone" covering the apex of the plug, a number of which successively form in

the quill portion as the dermal plug recedes, is in relatively remote association with the dermal plug activity. The former, however, far from suffering any cystine gradient effect, will tend to be suffused with more than adequate supplies from the blood stream and may even serve in a sense, as a more effective repository for removal of local concentrations of protein and other products, which in slower growing structures would be carried past the active growth zone by the circulatory system.

The feather interior would be expected therefore to show contrasting chemical composition with other epidermal structures like wool and hair, quite apart from the expectation that dermal and epidermal tissue formations would be distinct in accordance with the purely ectodermal origin of the latter.

As a step towards elucidating this point, a survey by the writer's colleague, Mr. J. Barritt, of the make-up of typical dermal and epidermal structures is in progress, and a few preliminary results for sulphur content are given below:—

Keratin.	Per Cent. S. on Dry Weight.
Hen feathers—barbs	2·70 2·33 2·51 1·47 2·59 1·87 0·74

Fuller information on these will be published shortly.

More definite evidence will probably be yielded from the aminoacid make-up. It is generally agreed that a certain number of amino acids, nineteen or so, are essential to complete body growth and development. It is unlikely, however, that all of them are necessary for each of the three fundamental ecto- meso- and endo-dermal activities concerned, still less that they are in the same proportions, though a survey of the literature does not indicate that the question of any special aminoacid requirements of dermal as opposed to epidermal formation has received attention.

One factor especially relevant, however, is the fate of glutathione. Indeed, if a primary basis behind the development of the nutritional aspect could be advanced it would trace back to the classical researches of Hopkins and his co-workers on the rôle of glutathione in animal tissues. It is this complex of cysteine, glutamic acid and glycine in equimolecular proportions, existing in the blood to the extent of 100 mgm. per 100 c.c., which is concerned, rather than cystine itself, in tissue metabolism. Wool substance yields cystine and glutamic acid in roughly equimolecular proportions, but glycine in relatively insignificant quantity, suggesting that it is primarily required for dermal elaboration, which latter, on the other hand, largely rejects the cystine component essential to epidermal elaboration.

Returning to the main point of sulphur content of wool, it will be admitted that the rôle of glutathione itself, in the elaboration of tissue which is so rich in glutathione residues, whether direct or indirect, must be of high importance, and the factors governing the autoxidation of such thiol bodies may be usefully reviewed as bearing on this problem.

The aerobic oxidation of —SH groups does not appear to fit in with any simple theory of catalysis,8 but whether cysteine is entirely nonautoxidisable if free from metals,9 or can autoxidise at very slow rate in spite of absence of iron, 10 the important accelerating effect of iron in this respect is well established. The similar acceleration of the glutathione autoxidation in presence of iron has been shown to be more complex in character, requiring an auxiliary catalytic factor.11 The earlier "deliquescent" preparations could be de-activated by a kaolin suspension, which absorbs the iron, whereafter addition of iron re-activated them. After absorption on muscle tissue, however, no re-activation occurred on adding iron, showing that an additional factor had also been removed. When the crystalline preparation was made available, it was found that after kaolin treatment it was not activated by iron, so that the auxiliary factor was not present. It makes its appearance, however, on long standing of an aqueous solution of the crystalline product, and this appearance is accompanied by the liberation of a small quantity of free cysteine. Since iron can form active complexes with cysteine, but not with the cysteine peptides, it is held that the amino group of cysteine must be left free for the iron catalysis to occur, and the cysteine impurity is regarded not as acting by the alternate oxidation and reduction of its own sulphur group, but merely as converting the iron into a catalytically active complex. It is the sulphur group of the glutathione which undergoes alternate oxidation and reduction in presence of tissue, the ferro cysteine (or similar complex) catalysing the reaction between glutathione and oxygen, its rate being thus limited primarily by the quantity of this auxiliary factor.

It is further stated that while cysteine closely imitates the properties of the catalytic impurity in "deliquescent" glutathione, it does not bring up the activity of the crystalline product to the expected value, since 8 per cent. of free cysteine requires to be added to produce the activity of the impure product, which, however, does not contain more

than I per cent. of cysteine according to the Sullivan test.

Thus although the evidence is circumstantial in character it definitely suggests the presence, in small quantity, of a thiol body other than cysteine, concerned in autoxidation, and possibly included in the keratin complex, and the analytical figures for cystine and total sulphur in wool, while showing that cysteine accounts for substantially the whole of the sulphur, do in fact indicate that a small residue is still unaccounted for. The only other thiol acid so far identified in wool is methionone, <sup>12</sup> which has been shown by synthesis <sup>13</sup> to be  $\gamma$ -methyl thiol  $\alpha$ -amino butyric acid. A later synthesis <sup>14</sup> has made it available in quantity. It has been found to be almost as efficient as cystine in increasing the growth of rats, and further investigations are promised <sup>15</sup> which will show whether cystine and methionone are interchangeable and utilisable for the same purposes, or if they are both "essential" amino-acids in which the basal Sherman-Merrill diet is deficient. It may possibly constitute the above auxiliary factor, despite the fact that it has no free sulphydryl

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Weichselbaum and Stewart, Nature, 28th May, 1932.
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group. A further thiol body, ergothionone, a betaine of thiol histidine, <sup>16</sup> is present in the blood corpuscles in appreciable quantity, and though its presence has not been observed in wool, this might be suggested, both from its labile SH group and as a possible primary source of the small quantity of histidine (0.6 per cent.) found in wool keratin.

Again, the presence of iron in wool substance would seem not to

Again, the presence of iron in wool substance would seem not to be adventitious, but evidence of ferro cysteine (or similar complex) activation. On this assumption, the approximate quantity can be theoretically computed; I per cent. of auxiliary factor on the quantity of glutathione giving a 13 per cent. cystine content in the wool would require 0.08 per cent. of iron. Determinations for wools of varying sulphur content carried out by my colleague Mr. E. Hill, by colorimetric estimation with thioglycollic acid, are given below:—

TABLE I.

Wool.	1	Per Cent. on Dry Weight.						
, , , , , , , , , , , , , , , , , , ,	Ash.	Sulphur.	Iron (as Fe).					
Australian merino A. A. A. A. A. F. A. F. F. South African merino C.  A. F. F. C.  South African merino C.  C.  C. C. C. C. C. C. C. C. C. C. C	6 85 85 86 87 87 88 86 87 88 86 87 87 87 87 88 87 87 87 87 87 87 87 87	3.91 3.46 3.46 4.11 3.53 3.94 3.67 4.01 3.10 3.22 4.01 3.34	0.010 0.00816 0.0082 { 0.0054 (1] 0.0060 (2) { 0.0051 (1] 0.0056 (2) 0.0042 { 0.0035 (2) 0.0035 (2) 0.0031 (1] 0.0028 (2) { 0.007 (1) 0.0054 (2) 0.0010 0.0041 (1) 0.0038 (2)					

These reveal no relation between sulphur and iron content; also the latter is only a fraction of that required for normal "impure" glutathione activity, suggesting that so far as iron is concerned the rate of any glutathione autoxidation involved in keratinisation would be, as might be expected, much slower than that in ordinary living tissue activity.

It may be remarked in this connection that though the essential requirement of available iron in hæmoglobin regeneration, an essential condition to general body growth, has long been recognised, it has recently been shown <sup>17, 18</sup> that highly purified iron produces only a very slow (though unmistakable) increase in hæmoglobin concentration, and that copper in minute quantity is an exceedingly potent and essential supplement to the iron in hæmoglobin building.

The significance of copper has also been emphasised <sup>19</sup> in the catalytic oxidation of cysteine, especially its increased activity in presence of

<sup>&</sup>lt;sup>16</sup> Barger and Evans, J. Chem. Soc., 99, 2336, 1911.

<sup>&</sup>lt;sup>17</sup> Waddell, Steenbock and Hart, J. Biol. Chem., 84, 115, 1929.

<sup>18</sup> Mitchell and Miller, J. Biol. Chem., 92, 421, 1931.

<sup>&</sup>lt;sup>19</sup> Elvehjem, *Biochem. J.*, 24, 415, 1932.

pyrophosphate, which destroys the activity of iron, and the probability again pointed out, in view of the universal distribution of copper in minute quantities, in all plants, and in the liver, muscle, and most animal tissues, that it is a biological requisite, particularly in situations where pyrophosphate is present, e.g. in muscle of certain animals, in yeast, and in blood. The copper content of wool, about 8 mg/kg <sup>20</sup> is very low compared with iron.

The follicle has no lymphatic clearing mechanism and no back flow takes place of fluid transfused through the papilla walls, in which catalytic agents follow with the transfused amino-acid components of the wool cells, and these, as shown in the succeeding paper, do not become kera-

tinised until well up in the follicle.

Thus the question as to such catalytic influences in the successive stages of keratin formation is extremely complex, yet the suggestion is ventured that measurement of the oxygen up-take of reduced wool hydrolysate might afford a practical comparison of the net catalytic activity, and hence a possible basis for comparison of different wool growths.

Proceeding to the more quantitative aspect of sulphur conversion into wool, it is of interest at the commencement to recall that in the discussion of a paper read at the British Association Meeting in 1927,<sup>4</sup> pointing out the importance of sulphur sufficiency in wool growth, the query was raised as to how far the soil-sulphur might influence the sulphur content and quality of the wool. Its extreme significance will appear later.

Shortly afterwards an extensive scheme of nutritional investigation was proposed in Australia by the late Dr. Brailsford Robertson <sup>21</sup> based on two assumptions: the constant content of sulphur, existing wholly as cystine, in wool, and the "essential" rôle of cystine in animal metabolism, an admirable review of which has been compiled by Marston. <sup>22</sup> The first was opposed to prior findings and erroneous, but this did not of course invalidate the general grounds for nutritional investigation on what then appeared sound biochemical principles—the repeated and generally accepted proof that cystine cannot be synthesised by animals from other sources of sulphur, and that their cystine requirement must therefore be obtained by them pre-formed in the diet.

"It is not," he said, "the withdrawal of sulphur from the soil which is the crucial factor in wool production, but the provision of cystine by the pasture... it follows that the carrying capacity of any country for sheep may very probably be determined by the capacity of its pasture plants

to produce cystine."

His deduction that for Merino sheep eight to twelve times as much pasture protein was required to produce wool as to produce flesh, and his computation of the protein required to supply the necessary cystine, even if the latter were quantitatively utilised in wool formation, led him to visualise in cystine deficiency a serious menace to the Australian wool-growing interests, and to advocate schemes for supplementing the pasture diet with cystine preparations, and a pasture survey, with a view to possible cultivation of pasture plants of higher cystine content.

р. 13.

Cunningham, Biochem. J., 24, 1267, 1932.
 Robertson, Commonwealth of Australia Coun. Sci. and Ind. Res. Bull., 39, 11, 1928.
 Marston, Commonwealth of Australia Coun. Sci. and Ind. Res. Bull, 39,

The interest of many workers in nutritional research has been directed to the hair-growth aspect of cystine deficiency, without however affording analytical evidence as to the sulphur retention in the hair. Attempts to influence the sulphur content of rabbit hair <sup>23</sup> by additions of cystine and of wool hydrolysate to a normal ration failed, as although between two successive three-months clip the hair from an individual rabbit increased by as much as 18 per cent. in sulphur content, with a decrease rather than increase in weight of clip, this was equally observed in the control and cystine fed animals, suggesting that the normal diet was cystine-sufficient and that the seasonal factor was predominant.

The striking evidence afforded in a recent paper <sup>24</sup> on the effect of cystine supplement on the rate of growth and cystine content of hair

in young rats, therefore calls for review.

A cystine supplement to a cystine-deficient ration (8 per cent. meat protein) gave relative increases of 7.2 per cent. in body-weight, 26.2 per cent. in hair-weight and 28 per cent. in cystine content of the hair.

An 8 per cent. wheat protein diet, presumably not cystine-deficient, gave no appreciable change with cystine supplement. A heavy protein diet (20 per cent. meat protein) showed no relative effects of supplementary cystine on cystine content, but a striking increase in hair production over the former diets. A lysine supplement to wheat protein diet gave a 17 per cent. increase in body-weight, and a proportionate increase in hair-weight, without affecting the cystine per cent. in the hair.

Re-expressing the averaged results in terms of 100 grm. for body-

weight some significant points emerge:-

In diet (I) there is a striking increase of 17 per cent. in hair growth per unit body-weight, and 33 per cent. in total hair-cystine produced, 53 per cent. of which is accounted for by the increased per cent. of cystine in the hair.

Diet (2) shows no important relative change, but emphasises the

low hair yield on substituting wheat protein for meat protein.

Diet (3) also without any relative changes due to the cystine supplement, shows a marked increase in hair and hair-cystine yields per unit body-weight even over (1) with cystine supplement.

Diet (4) shows in addition to the above-mentioned improvement in actual body and hair weight over the lysine-deficient wheat protein diet, a significant increase in hair yield per unit body-weight with the lysine

supplement.

Thus "while any amino acid may stimulate hair growth if added to a basal diet whose general growth-promoting power is increased, an effect on the cystine content of hair results only when a cystine-deficient diet is corrected by a cystine addition. The cystine-deficient diet produces a hair deficient in cystine; the effect is removed by adding cystine to the diet until the cystine deficiency has been satisfied. Hair with a normal cystine content is thus produced. Additions of cystine to diets possessing such sufficiency, however, have no certain effect upon hair composition. The production of a hair coat containing a super normal cystine content does not seem to result from the feeding of excessive amounts of cystine."

This statement is qualified by the fact that there is no evidence of "normal" cystine content being a fixed quantity for a given type of

Barritt, King and Pickard, Biochem J., 24, 1061, 1930.
 Smuts, Mitchell and Hamilton, J. Biol. Chem., 95, 283, 1932.

hair coat, or even for an individual animal, still less for an individual fibre. These workers point out that it is inconceivable that there could be any modified composition of the individual proteins by diet changes; rather there is a disturbance of the normal ratio of proteins in the hair fibre with cystine-deficient diet, giving a greater proportion of proteins poor in cystine. They advance microscopic evidence of this from the appearance of abnormal hairs present in the coat under these conditions.

The medullary cells are less regular and occupy a greater proportion of the hair shaft, with a correspondingly smaller proportion of cortex, and they explain the lower cystine content on the assumption that the medullary substance is, as has been proved for wool medulla, relatively poor in sulphur.

In view of the enormous increase in 3a against 1a (see Table II) of 78 per cent. in cystine yield per 100 gms. body-weight, and 35 per

						Hair Yield. Gms.	Cystine Content. Per Cent.	Hair-Cystine Yield. Gms.
(1) 8 per cent. me. (a) No cystine (b) Cystine.			•	•	•	1·55 1·82	10·1 12·9	0·157 0·235
(2) 8 per cent. who (a) No cystine (b) Cystine .						1·28 1·34	13.2	0·169 0·177
(a) No cystine (b) Cystine .				•	•	2·09 2·00	13.3	0·278 0·268
(4) Wheat protein (a) No lysine (b) Lysine .	(8-10	per c	ent.)	•	•	1·48 1·58	13·6 13·2	0·185 0·180

TABLE II.

cent. in hair yield, though the average body-weights in these series were practically identical, the importance of general nutritional factors apart from cystine sufficiency, purely from the hair-growth standpoint, is strikingly demonstrated so far as the metabolism of the rat is concerned.

The quantitative significance of the data given is qualified by the circumstance that the whole coat, and not merely the portion grown during the diet periods, was analysed; also they would not necessarily hold over indefinite periods where there is not the steady growth characteristic of sheep's wool. (The merino follicle is known to produce a continuous fibre with the same yearly lengthening over three years' growth.)

They do, however, effectively demonstrate that the *composition* as well as the *yield* of hair is subject to nutritional influences, which has been the standpoint of the writer and his colleagues since 1926 regarding wool.

Thus if the diet is only cystine-deficient, a lower yield of wool with low percentage of sulphur will result; if cystine-sufficient, but for example lysine-deficient, a "normal" sulphur content with lower yield of wool would be expected. There has, however, been no suggestion that sheep pastures may be deficient in any particular essential aminoacid other than cystine, and with the concentration of attention on the

latter, the speculations as to the prospect, if any, of its deficiency in the natural foodstuffs available to the sheep have recently given way to definite evidence from analytical investigations of the forms of sulphur they contain.

From the figures 25 tabulated below:-

TABLE III.

	Gras	ss.			Per Cent. Water.	Per Cent. Total S.	Per Cent. Sulphate S.	Per Cent. Organic S. (Diff.).
Cocksfoot					75	0.44	0.31	0.23
Perennial rye		•			77°I	0.46	0.23	0.23
Prairie grass		•			80.0	0.59	0.34	0.25
Yorkshire fog					77.0	0.39	0.13	0.26
Hair grass	•	•	•	•	73.3	0.32	0.10	0.25

there is no wide variation in organic sulphur. In the last two grasses, which are "worthless as regards pasture," it is in fact slightly higher. They are obviously, however, low in sulphate-sulphur, and Aitkin further infers that sulphate dressing of soils mainly increases the sulphatesulphur of the pasture. He could find no evidence of the presence of cystine.

Analyses of grasses at the Cambridge University farm 26 have yielded results somewhat higher, but in the same direction, for total and organic sulphur, and confirm the above effect of sulphate-sulphur dressing, the average increase in organic sulphur content of the grass being 8 per cent., compared with 25 per cent. in sulphate-sulphur.

Regarding seasonal variations, in relation to the sulphur availability, the following table compiled from the maximum and minimum sulphur contents in both dressed (A) and undressed (B) pasture, shows the marked extent of this variation (especially in inorganic sulphur) which further is quite out of step with the protein variation, suggesting that the

TABLE IV.

	Total	Approx.	Inorg.	Approx.	Org.	Approx.	Crude	Approx.
	S.	Period.	S.	Period.	S.	Period.	Protein.	Period.
Max. (A) Min. (A) Max. (B) Min (B).	1·16 0·72 0·93 0·57	July-Aug. AprMay July-Aug. AprMay	0.37	July April July April	0·48 0·30 0·44 0·28	Aug. June Aug. Apr May	25.07 18.67 24.6 17.3	March-April May-June March-April May-June

organic sulphur must be present in part at least as other than protein sulphur.

Regarding the cystine content, "attempts to isolate cystine from pasture grass have shown only a trace of the amino-acid to be present. The Folin method gave 0.22, 0.22 and 0.29 per cent., while the Sullivan method indicated only a trace of cystine present." The conclusion is made that the cystine content of grass must be less than O·I per cent.

Aitkin, Biochem. J., 24, 250, 1930.
 Evans, J. Agric. Sci., 21, 806, 1931.

of the dry matter (corresponding approximately to 0.025 per cent. of sulphur or 0.006 per cent. in fresh grass) and that some precursor of cystine is present in grass which can be converted into cystine in the animal body.

This receding from the conception of cystine itself as a food essential still carries the inference that the organic sulphur is the limiting factor, though this is against the indication from the "worthless pastures"

of Table III.

Further data on this point, from South African pastures and bushes,<sup>27</sup> show that only very small amounts of cystine, if any at all, are present, and though certain bushes contain considerably more total sulphur than do the grasses, this is mainly in inorganic form, and the organic in other than cystine form. The latter, even when the plant is in active growth, only reaches '02 per cent.

Either the inorganic or organic sulphur contents would be amply sufficient for wool requirement, but hasty calculations already published to prove the inadequacy of cystine availability, from still indefinite information, both as to true cystine content and food consumption, are

in wide disagreement.

Rimington and Bekker <sup>28</sup> quote an annual yield per sheep of 6 lbs. clean wool, equivalent to 0.78 lb. of cystine, or 0.2 lb. sulphur, on 4 lbs. fresh pasturage, equal to 1.43 lb. dry matter per day, *i.e.* 522 lbs. per year, requiring 0.038 per cent. S as cystine on dry matter, were all the cystine utilised.

Henrici's estimate of 5 lbs. clean wool from 5 lbs. of dry fodder per day, requires 0.0093 per cent. S as cystine on dry matter, one fourth

of the above.

The average Australian merino has a clean fleece weight of 3 lbs. (Robertson) equal to a production of 0·I lb. sulphur per annum, which, assuming a daily ration of 5 lbs. fresh pastures of 75 per cent. moisture content, would require 0·022 per cent. S as cystine on dry weight.

From approximate information regarding English crossbreds it would seem that a 5 lbs. clean fleece weight results from a ration of about 3½ lbs. dry matter per day, requiring 0.013 per cent. sulphur as

cystine.

Thus Evans' maximum estimate of 0.025 per cent. sulphur as cystine in dry fodder would (excluding Rimington's figure) be sufficient for the fleece production were it completely utilised. Henrici's estimate in fact would require under 40 per cent. to be retained for wool production.

While it seems highly probable that the actual cystine-sulphur is well under this maximum, it must be less than half this figure to exclude entirely, on the above calculations, the possibility of actual cystine sufficiency, without reference to its degree of retention for wool formation.

There is at present no information on the latter point, nor can any of the work done on cystine feeding to other animals, from the standpoint

of sulphur retention, be safely applied.

Apart from that lost by excretion, and that utilised in general body growth, the follicle itself ejects an appreciable amount in the shed inner root sheath (which is no doubt responsible for the sulphide produced in stale scouring liquors).

Henrici's figure, however, of 0.02 per cent. cystine as the maximum ever reached, even in the sulphur-rich karroo bushes, renders argument

Henrici, Farming in South Africa, April, 1932.
 Rimington and Bekker, Nature, 7th May, 1932.

as to the percentage retention superfluous, this quantity being hopelessly inadequate to account for wool production from any pasturage.

Also the full report of the Meteor Downs experiment in Central Queensland, now available, <sup>29</sup> constitutes in effect a withdrawal from the position previously taken up in that quarter regarding cystine deficiency. The natural pasture there, "which during many months is deficient in protein," the protein content at the end of the dry winter often falling below 1.5 per cent. of the dried grasses, was supplemented by blood meal, consisting of 80-85 per cent. protein, and containing 2.6 per cent. cystine, 4.1 per cent. arginine, 3.5 per cent. histidine and 6.0 per cent. lysine.

Marked improvement in wool yield and quality resulted. In the first year of experiment the average fleece weight was 110.9 oz. in the supplement group and in the control group 80.9 oz.; in the second year 130.3 against 95.6, but the sulphur contents of the wools are not recorded.

The recovery of cystine from the supplement taken, in the form of increased fleece, is given as being of the order of 35 per cent. The control animals maintained their body-weight over the period of nutritional stress.

The question must be asked—would not this protein-rich concentrate, minus the cystine, have produced the same result, and is the experiment that of adding a cystine supplement to a cystine-deficient but otherwise adequate ration, or merely that of raising the generally low nutrition level?

The sulphur content of the grasses is omitted from the table of determinations of mineral constituents, but there is little doubt, from the values previously quoted, that their non-cystine sulphur, together with that in the stockwater, would meet the sulphur demand for normal wool production, even in the periods of excessively low protein content of the grasses.

The problem has been made much clearer by the recent work of Rigg and his co-workers 30 at the Cawthron Institute, following on that of Aston, 31 on "Bush sickness" in New Zealand. The iron deficiency causing this ailment, which in severe cases results in practical cessation of wool growth, is due to deficiency of available iron in the soil ingested with the pasturage, the latter being iron-deficient in "healthy" and "unhealthy" areas alike. The average seasonal iron content of the pasturage on a typically "unhealthy" area was 0.008 per cent. Fe, and 0.009 and 0.011 on the two healthy areas examined.

The soil-iron contents, however, are very significant as regards "soluble" iron, and are therefore quoted in detail:—

TABLE V.

Soil Type.		Total Iron.	Iron Sol. in 5 Per Cent. Oxalic Acid.
Hamilton, healthy Te Kauwhata, healthy Montere hills, healthy Taupo, unhealthy Kaiteriteri, unhealthy		8·1 6·74 3·09 3·20 0·83	3·72 4·65 2·8 0·66 0·41

<sup>&</sup>lt;sup>29</sup> Marston, Commonwealth of Australia Coun. Sci. and Ind. Res. Bull., 61, 1932.

 <sup>&</sup>lt;sup>30</sup> Rigg and others, N.Z. Dept. of Sci. and Ind. Res. Bull., 32, 1932.
 <sup>31</sup> Aston, Trans. N.Z. Inst., 58, 536, 1928, and later papers.

With the soil contamination, approximately 0.4 per cent. of the pasture weight, the percentage of total available iron on dry matter becomes:—

Kaiteriteri o·o136 (as Fe) o·o19 (as  $Fe_2O_3$ ). Montere Hills o·o482 (as Fe) o·o69 (as  $Fe_2O_3$ ).

The former supplemented value is still very low in comparison with normal iron contents of pastures. Wolff <sup>32</sup> found for the Fe<sub>2</sub>O<sub>3</sub> content (on dry matter) from twelve species of pasture plants, the lowest value was 0.01 per cent. and the highest 0.1, with an average of 0.042. Orr <sup>33</sup> quotes for rye grass (Aberdeenshire) 0.05 per cent. Fe<sub>2</sub>O<sub>3</sub> and for clover 0.07.

Marston's values for the Queensland fodder plants are therefore of especial interest.

Per Cent. on Dry Matter. Species. Protein. Fe<sub>2</sub>O<sub>3</sub>. CaO.  $P_2O_5$ .  $N \times 6.25$ . A. Chloris pectinata, green shoot three 5.6 0.04 0.42 0.14 weeks after "burning off" B. Andropogon species, green shoot three weeks after burning. 8.7 0.58 0.72 0.71 C. Andropogon, green leaves, 6 ins. 6.2 0.82 0.03 0.32 high, unburned area. D. Andropogon, leaves from plants 9 0.02 0.61 0.38 5.2 ins. high, unburned. E. Glycine tomentosa, off burned area. 0.26 15.0 2.07 0.55

TABLE VI.

These clearly indicate that iron is second only in demand to protein. The rejection of (A) is no doubt additionally due to the low calcium and

phosphorus content.

The level at which the "bush sickness" anæmia disappears is between 0.02 and 0.07 per cent. Fe<sub>2</sub>O<sub>3</sub>; the latter is that of clover, already quoted. There is as yet no evidence that even this figure (roughly 0.7 gms. per day), in the healthy areas, represents the full iron sufficiency for maximum wool growth in addition to body growth, yet this is well above that of those Queensland grasses rejected when the iron-rich pasture is available. These deductions support Rigg's suggestion that in the Meteor Downs experiments the iron supplement (0.2 per cent. in whole dried blood) in the blood-meal administered was the significant factor. The unusual importance in the case of sheep of the iron auxiliary to an otherwise generally satisfactory mineral content is reflected for example in the high iron content in sheep's milk, 0.0079 per cent. against 0.00014 in that of the cow and 0.00007 in that of the mare.<sup>33</sup>

From experiments at the Onderstepoort Government Farm, South Africa, on direct administration of sulphur to sheep, increases have

<sup>(</sup>E) is taken by the sheep in preference to all others; the newly grown shoot of andropogon (B) is preferred next; the others are left practically untouched, while the former are abundant, and (A) is left while there is still andropogon available.

<sup>32</sup> Wolff, Aschen Analysen, 1880.

<sup>33</sup> Orr, Minerals in Pastures, 1929 (Lewis).

been reported averaging 12.2 lb. in body-weight and 2.95 lb. in fleece

weight over the control group.34

Thus the circle of investigation bearing on sulphur utilisation by the sheep, though in its course contributing valuable new information and ideas on nutritional matters, would seem to have closed upon the starting-point of inorganic sulphur availability as the true limiting factor in wool growth.

A new aspect has thus developed—what are the factors favourable

to the sheep's conversion of non-cystine sulphur into cystine?

The rumen mechanism, an unstudied factor from the essential aminoacid standpoint, appears to place the sheep outside all accepted views on this subject, and explain its known ability to produce wool more or less normally after subsisting on poor pastures over long periods.

The results of the promised diet investigations, keeping a cystine and sulphur balance-sheet, to test the hypothesis that intestinal bacteria are responsible for transforming sulphates into cystine <sup>28</sup> will therefore

be awaited with great interest.

On this hypothesis the catalytic effect of iron primarily in invigorating such bacterial action and increasing its synthetic efficiency, 35 thus involving an additional iron demand, may be no less important than its established general rôle in arresting and preventing those anæmic conditions which, in the case of sheep, are at once reflected in poor yield and quality of wool.

In conclusion it may be pointed out that the nature of the birthcoat of the merino lamb would seem to be of peculiar significance in relation to this discussion. There is evidence that the first fibre growth during feetal development is largely medullated and hairy, giving at birth the hairy birth-coat found in many types of sheep, e.g. the merino.

This birth-coat persists for a few months but gradually gives place to the adult type of coat, which in the merino consists substantially of non-medullated true wool fibres. The metabolism concerned in the lamb's early post-natal life, maintained on a milk diet, is presumably like that of the rat, subject strictly to accepted essential amino-acid considerations. Its diet is apparently cystine-deficient in respect of the coat, and it is unable to acquire any cystine supplement.

With the development of the rumen, the system for obtaining cystine becomes revolutionised to that of the ruminating herbivore, and the animal is no longer dependent upon pre-formed cystine for wool growth.

Thus regarded, this affords the most striking instance of the extremes of variation possible, in one and the same animal, during its lifetime, in sulphur economy.

<sup>&</sup>lt;sup>34</sup> Pastoral Reveiw, 16th May, 1932. <sup>35</sup> King, Nature, 11th May, 1932.

## CHEMICAL CONSIDERATIONS IN RELATION TO THE STUDY OF MAMMALIAN HAIR GROWTH.

## PART. II.—OBSERVATIONS ON THE CHEMICO-HISTOLOGICAL SYSTEM IN FOLLICLE ACTIVITY.

By A. T. King and J. E. Nichols.

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The typical covering of mammals consists essentially in fibres, which, while exhibiting great variations in macroscopical form and in the arrangement of their constituent cellular residues, conform in general to a relatively simple plan of construction. This has been described by numerous authors and attempts have been made to classify fibre types according to the proportions of the constituent layers (e.g. hair-wool), the time of growth (kemp-wool) and the form of the cuticular scales. Further the regional variations in fibre characters on the individual animal have been examined in several species. The histological details of the follicle and its fibre product have also been subjected to examination (vide Danforth, Duerden and Ritchie, Maximow, Wildman, etc.).

Much uncertainty yet remains as to the system by which the follicular elements become differentiated into the fibre layers and as to the precise nature of the changes involved in keratinisation. (For example it is not yet absolutely clear whether the "medulla" is derived immediately from cells of the basal layer towards the apex of the papilla or includes also cells from the region of the slopes of papilla or again

includes also papillary, dermal residues.)

The fact that complete fibres which are strongly medullated in portions of their length, have tips and roots which do not include medulla, may be significant in relation to the subsequent discussion. The main features common to all follicles whether they produce medullated or

non-medullated fibres may be briefly stated as follows.

Within the connective tissue sheath and its hyaline membrane which delimits the dermal structures surrounding the follicle, the basal layer of the stratum Malpighii (A in diagram) is continued around the follicle neck and bulb and invests the dermal papilla. The other layers of the epidermis do not exist in the follicle below the level of the opening of the sebaceous gland. They are replaced by a more complicated system of distinct sheaths which originate apparently in a localised mass of undifferentiated epithelial cells which occupies the moat-like depression or fold around the papilla and closely surrounds the pedicle and lower slopes of the latter. (See Plate I.)

From the cells of the growing zone the structures of the inner root sheath and the fibre are elaborated and become differentiated in a more

or less well-defined succession.

The (dermal) papilla contributes no cellular elements to the stream of epithelial cells which passes outwards and upwards, with the possible exception of dermal cell residues or debris from its apex in the case of

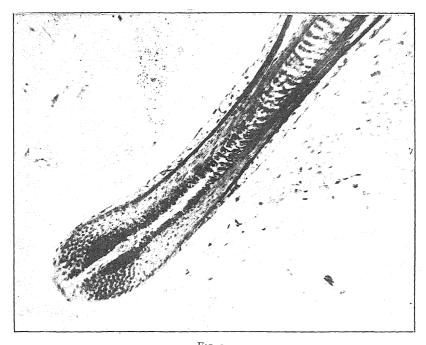
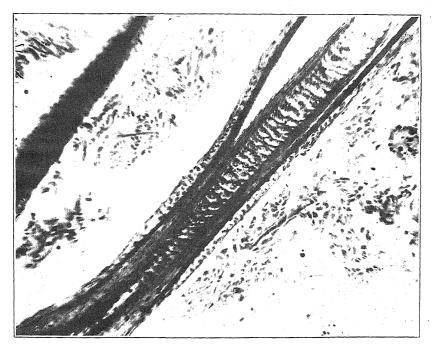


Fig. 1. Section of guinea pig hair follicle,  $\times$  250, stained saffranin and picro-indigo carmine, owing growing zone and development of the various layers.



 $\label{eq:Fig.2.} \textbf{Fig. 2.}$  Showing separation of inner root sheath from formed fibre.

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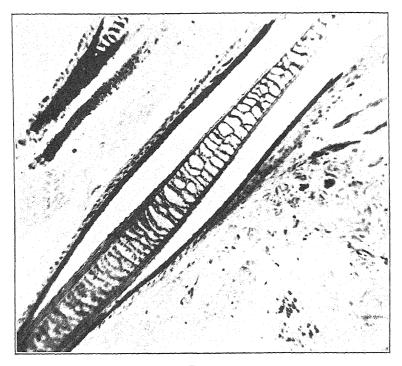


Fig. 3.

Illustrating subsequent changes in the formed fibre; desiccation of medullary cell inclusions; relative constriction of cortex. Imbrications of the cuticle of inner root sheath and fibre cuticle can be seen, and in addition the later shedding of the inner root sheath.

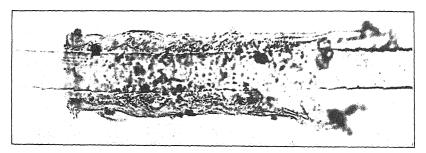


FIG. 4.

Non-medullated merino wool fibre,  $\times$  500, showing unusual case of shed inner root sheath fragment remaining in association with the fibre.

[See page 276.

follicles giving rise to medullated fibres. The independent nature of the papilla allows of the relation, for descriptive purposes, of the various levels of the follicular cell streams to the topography of the papilla.

Thus the lower portions of the stream of cells in the growing zone of the fibre, from the region of the lower third of the papilla give rise to—

(I) The Layer of Henle (one cell thick), which forms the outer layer of the inner root sheath and in which trichohyalin granules appear about the level of the middle of the papilla and keratinisation occurs about the level of the summit of the papilla. (B in diagram.)

(2) The Layer of Huxley: (C) in which some coarser granules of trichohyalin appear just above the tip of the papilla and which becomes

keratinised higher in the follicle, some distance from the papilla.

(3) The Cuticle of the Inner Root Sheath: (D) of flattened cells, keratinised from a short distance above the follicle bulb, i.e. higher or later, than the cells of the Huxley and Henle layers.

From the region of the sides of the papilla at or just below the middle

of its height, the cells arise which become differentiated as—

(4) The Cuticle of the Fibre: (E) the cells of which, while polyhedral when passing through the bulb of the follicle become flattened and "slated" one upon the other, being cornified higher up the follicle shaft, and later than the cells of the cuticle of the inner rootsheath their free outer margins appearing inter-digitated with the free, inner margins of those of the latter layer.

In the region of the upper half of the papilla, the epidermal cells become gradually elongated in the direction of the axis of the follicle and go

to form-

(5) The Cortex of the Fibre (F) becoming keratinised (according to Maximow) without the intermediate deposition of granules in the cytoplasm, some distance above the follicle bulb, in the higher reaches of the lower third of the follicle shaft.

In follicles which give rise to medullated fibres:—

(6) The Medulla (G) arises from the region of the higher slopes, and the summit of the papilla, the cells, probably largely due to their situation, being apparently constrained to move more directly upwards or axially to the follicle, than those which go to form the other fibre and the inner root sheath layers. They form a central column of large polyhedral constituent cells, in which granules of trichohyalin appear, and later, much higher in the fibre shaft, become cornified and shrink leaving comparatively large air-filled spaces.

At the region and time at which the fibre layers are all cornified they are surrounded by a system of concentrically arranged tubes of already completely cornified cell layers, *i.e.* by those of the inner root sheath. There also the hyaline membrane, limiting the epidermal structures of the follicle, is thick and immediately within it the outer root sheath is made up of more than one cell layer. Hence the organised fibre substance can probably be considered almost entirely occluded from *lateral* 

sources of nourishment or fluid medium. (See Plate II.)

Before discussing the chemical significance of this orderly sequence of development of inner root sheath, fibre cuticle and cortex, the fact, frequently overlooked, must be emphasised that normal fibres do not consist solely of keratinised tissue, and nuclear residues from the original nucleus of each individual cell, the latter really being contaminating material from the standpoint of keratin composition. Each cell in the organised fibre has primarily emanated from a region, or matrix, in

which all the undifferentiated cells are bathed in a fluid plasma or nutritive medium, which must be carried into the follicle mechanism before being denuded of those protein constituents which form the fibre cells. The exhausted fluid might recirculate by a back diffusion into the blood stream, but would obviously tend chiefly to be conveyed upward within the follicle organisation, partly by bodily transference with each cell in its early, replete stages, and partly by capillary flow which would arise as the cells become contracted (and depleted), providing definite intercellular channels. This flow will naturally no longer occur once the cells have ultimately hardened by evaporation and the fluid suffusing them has dried up, depositing its solutes at the evaporation zone, in the intercellular cavities. Within the fibre the capillary flow would tend to occur in the intercellular spaces earliest formed as a result of keratinisation, i.e. in the cuticular-cortical margin and in the outer layers of the cortex.

The nature of these deposits is not as yet elucidated, but presumably will correspond to that of the plasma minus the keratin-forming constituents absorbed in keratin formation, plus any break-down or byproducts which may be associated with this biosynthesis. As an indication of the former, it is recorded (by Maximow, in man) that the following constituents are present: "... oxygen, nitrogen and carbon dioxide, proteins, carbohydrates, lipins, inorganic salts and a hetero-

geneous collection of organic substances.

"The proteins include fibrinogen, serum albumin and at least two globulins; amino-acids, and albumenoses are also present as such. Sugar is always present in fair amounts and may be greatly increased in certain diseases. The lipins of the plasma are neutral fats, cholesterol esters and phospholipins, including lecithin. The inorganic salts are a mixture of sodium, potassium, calcium and magnesium chlorides, carbonates, phosphates and sulphates."

Maximow also records, for the human hair follicle, that "lymphatic vessels are not connected with the hair or glands of the skin." Assuming that this mechanism for the removal of katabolised material is also absent from the immediate neighbourhood of the follicles in other mammals, e.g. the sheep, further support is lent to the argument that this

material has no organised means of exit from the follicle.

A few observations may be made here regarding the so-called "cementing medium" between the cells. It would seem that if such a medium were being laid down or elaborated specifically by the cells it would appear while they were still living, *i.e.* in the lower parts of the follicle and its bulb. If its deposition were the result of the dehydration of the tissues, in such a system as that of the follicle and fibre it would coincide with the deposition of the "contaminating" materials described.

With the closer approximation of the cells, the fluid in circulation in the intercellular spaces will be attracted to the cell contact areas, but with increasing pressure of contact owing to the constriction of the fibre perimeter, this liquid at and near the points of contact will be practically forced out to the regions where the cell surfaces are in less close proximity. Such spaces obviously must occur in the packing of spindle shaped (cortical), or irregularly flattened (cuticular) cells, particularly, and in them would occur the ultimate deposition or precipitation of the "cementing medium."

Whatever the precise nature and effect of this "cementing" layer its origin, above suggested, agrees with such observations as those of Allworden and Rimington who have isolated material of carbohyemdr nature, Waters who has implied it to be easily removed by enzatey action, Burgess who has examined the water-soluble nitrogenous extract in relation to susceptibility to bacterial attack, and on the considerable ash content of wool and similar growths.

The presence of the spiny processes described by Duerden in the medulla of Merino kemp, might tend to interfere with the movement of fluid indicated above and might possibly ensure a greater measure of continuity of the keratin structure of the fibre.

The adhesion between one cell and another is better explained by the contractile forces which, so to speak, glue together the semi-plastic cells, in addition to which chemical forces will come into play through polarity effects between the adjacent protein surface layers.

Having discussed this aspect of internal contamination it is worth while examining to what extent the sebaceous and sweat glands could contribute. It may be thought that there is an internal lubrication of the fibre (keeping it supple) by fatty material derived from the fat gland itself; also that fibres harshened, it is presumed, by loss of suint, are restored to their original handle by "feeding" in a suint emulsion.

There is actually a fat gland associated with each individual follicle, though not necessarily a sweat gland, which may be of significance.

The orifice of the sebaceous gland, however, is definitely at a level

The orifice of the sebaceous gland, however, is definitely at a level above that at which the fibre structure is complete and therefore its secretions are applied *only* to the outer surface of the fibre. Any fatty material internal to the fibre must, therefore, have been accumulated either from the plasma flow above described or by penetration of the gland secretion through the fibre cuticle. The latter is ruled out on the one hand by the molecular complexity of such compounds as constitute wool fat being, according to Speakman, too great to allow penetration of the micellar spaces and on the other by the fact that the internal fatty matter is quite different in character from wool fat.

Speculation can be made as to the effects of the application of fatty secretions to the surface of the fibre as it emerges from the follicle, postponing evaporation, *i.e.* raising the level of the evaporation zone, and/or reducing its rate. With continued fibre growth neither would affect the ultimate amount of deposition of internal contaminating materials, but the latter would involve the deposits being formed in a more emulsified or colloidal state than by sudden precipitation.

Such a retardation of evaporation, or deposition, might be a contributing factor to the different handle of growing wool under certain circumstances. It is sometimes claimed that in fleeces where a steady even flow of grease, or yolk, is maintained the wool exhibits a softer handle and more lustre than in those where the grease flow ceases low in the staple; and further that these conditions remain in the wool after washing or scouring. In so far as fibre pliability may be involved in handle, especially of growing wool, this would possibly be influenced by the condition of deposition of the contaminating materials.

The sequence of differentiation (or development in the keratinised sense) of the layers of the inner root sheath, the fibre cuticle, cortex and medulla has been described. The inner root sheath and fibre move upwards continuously and simultaneously, the serrations of the cuticle of the inner root sheath and that of the fibre being virtually interlocked. The order of the formation of the layers implies the same order of availability of building materials from the blood stream; in other words a

gradient in their supply. In view of the special function of sulphur in the form of cystine regarding fibre formation, this may be more simply examined by postulating a cystine gradient in the direction of the "involution" of the papilla boundary. (While the cystine is presumably present in the medium in peptide form, rather than free cystine, the term "cystine gradient" will be used for convenience.) This assumption is reasonable in view of the shape, structure and disposition of the follicle in its seating in the dermal tissues which would influence the relative availability of cystine to the layers in accordance with the proximity of the various parts to the nutriment stream. Arguing on physico-chemical lines, the cystine concentration in the blood and its rate of flow, as well as the varying forms of papillæ, would also influence the initial availability of cystine to the various parts of the follicles.

The inner root sheath is, from the histological evidence, the first of the follicle products to appear in a developed form and it must be assumed that as it is an organised product of follicular origin, cystinisation is at least as much involved in its formation as in that of the constituents of the fibre itself. There is, however, no analytical evidence regarding its composition; also it is continuously shed with the outgrowth of the formed fibre (see Plate III.), and may therefore be omitted from the present discussion of the fibre substance.

Reference to the diagram shows that, next to the layers of the inner root sheath, the cell stream originating closest to the nutriment stream is that which follows along the inner root sheath already laid down and goes to form the fibre cuticle. The cells of this layer would receive their quota of sulphur involved in their cystinisation before those further removed from the main nutritive stream and higher up the cystine gradient. The cuticle mass in relation to the total fibre is relatively small, hence the quota taken by the cuticle is practically independent of the quantity remaining available for the other fibre structures.

The fall in the sulphur gradient due to absorption by the cuticle cells is correspondingly small, but its effect on the cystinisation of the cortical cells (next in succession in the gradient to the cuticle cells) is magnified by the proportionately large number of these which have to draw, for their quota, from the partially depleted cystine stream.

A higher cystine content may therefore be anticipated in the cuticle than in the cortex, but this is not necessarily so, since the cuticle quota might be satisfied without excessive sulphur absorption. Though actual analyses of sulphur content of scale and cortex have not yet been made for wool, Chamberlain records no appreciable difference between these two fibre "layers" so far as human hair is concerned.

between these two fibre "layers" so far as human hair is concerned.

The other typical amino acids, such as tyrosine, present in the fluid bathing medium, are likewise preferentially available to the cuticle cell stream; but these apparently take no part in the cuticle formation (in the keratinised sense) and are passed on to be included in the later developed fibre constituents. With cystine as a specific agent in keratinisation, the proportion of cells which would receive their quota for complete cystinisation, without the inclusion of any other alternative amino acid to produce general "cornification," would be limited, the rate of proliferation of cells in the growing zone in relation to the progressing depletion, by absorption, of the cystine supply—i.e. to the cystine gradient—being the limiting factor. The expectation would be therefore, with such a gradient, that the later "keratinised" fibre constituents would contain proportionately less and less cystine and more and more other residual amino acids and extraneous contaminating materials.

While precise information on the latter point is lacking, analyses show that the medulla, the last formed fibre layer, contains no cystine; and qualitative tests show, e.g. in the porcupine quill (Bekker and King) that while the cortex includes tyrosine and some histidine, the medulla gives an anomalous staining test indicating the presence of constituents foreign to both scale and cortex.

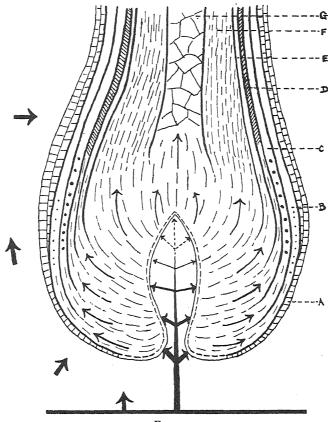


Fig. 5.

Diagrammatic sketch of hair follicle system.

The cystine gradient is represented by the arrows around the follicle and in

the papilla.

The arrows within the follicle indicate the direction in which the cells move to form the several layers B C D E F G (the boundaries of which are indicated by the heavy lines) within the outer root sheath A. The situations of the letters B, C, D E, and F indicate the relative positions (necessarily fore-shortened) at which keratinisation of the various layers occurs.

In conclusion certain wider problems concerning general and effective cystine availability in relation to different wool types may be briefly indicated.

For a given follicle the fibre/blood stream distribution coefficient of the cystine may be regarded as governed by the concentration of cystine in the blood and its rate of flow into the follicle. Presumably only the former is variable. Such variability, with consequent variation in cystine availability, obviously cannot be unlimited, and can only occur within the limits safe for the general health of the sheep.

A similar distribution coefficient effect will obtain with the other essential amino acids, whose concentrations in the blood stream also are similarly limited, though less critically, since whatever change may occur in yield of follicle product, this would not on our hypothesis be strictly in proportion to the variation in cystine absorption.

The genetic type and disposition of the follicle therefore remain the predominant variables concerned, *i.e.* even the *same* cystine quota available to adjacent follicles will be differently utilised according to their type. The fine slow-growing fibre of the adult Blackface coat would not be expected to develop a continuous medullary channel, nor its coarse rapid-growing fibre to lose it, under physiologically admissible variations of cystine concentration.

This discussion applies to hair growths generally and has been developed by collating evidence from many sources but more particularly

from the study of sections of guinea pig skin.

#### Acknowledgments.

The author gratefully acknowledges his indebtedness to Professor J. E. Duerden and Dr. J. E. Nichols for helpful discussions on the histological aspect, and to Mr. J. Barritt and Mr. E. Hill for their determinations of sulphur and iron recorded in Part I. of this paper.

In Part II., the authors have been fortunate in having access to the admirable sections kindly placed at their disposal by Miss D. H. Strangeways, to whom they also express their grateful thanks for her helpful comments.

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#### GENERAL DISCUSSION.

**Professor J. E. Duerden** (Leeds) pointed out the significance of the fact that for the first time the authors of the papers had made an attempt to understand the growth of the fibre in its relationship to the papilla, as the only nutrient source of the fibre. Fibres present a remarkable variability in thickness, length and other characters, both as regards the individuals in a sample and in each fibre separately, and a study of the differences in the papilla might yield a deeper understanding of these variations. He questioned whether the differential proportion in the amount of cystine postulated in the papilla was justifiable on physiological grounds.

Dr. Speakman (Leeds) said: The hypothesis of a cystine gradient, according to which "the cuticle might be expected to show the highest sulphur content and the cells forming the cortex to show progressive diminution in sulphur content with their distance from the cuticle layer," can hardly be correct in all its implications. Using a sample of human hair containing 5.02 per cent. of sulphur, Chamberlain has shown that removal of 15.3 per cent. by weight of the fibre by a process of descaling leaves the sulphur content unaltered at 5.02 per cent. In a second experiment where the loss of weight on descaling was 20.8 per cent., the sulphur content of the descaled hair was 5.04 per cent. Although these results may not be conclusive as regards the sulphur content of the cuticle, they seem to disprove the general hypothesis of a sulphur gradient from the outside of the fibre to the interior, at least in the case of human hair. For if the hypothesis were correct, the sulphur content of descaled hair must always be less than that of untreated hair, no matter what weight of fibre may have been removed by descaling.

Mr. King, in reply, said: From the review of the evidence of variation of cystine content of wool, not only as between different types, but along the length of the staple, it is difficult to avoid the conclusion that whatever may be the physiological reason, varying incorporation of the cystine nucleus must occur during wool growth. Nor would it seem that variations in cystine content of the magnitude observed—as much as 30 per cent.—could be safely disregarded from the structural stand-

point.

A sulphur gradient in the fibre from the outside to the interior could be expected from, but would not be a necessary consequence of, the cystine gradient postulated in the papilla, especially with high initial availability.

The negative evidence cited in the case of human hair could scarcely be accepted as applying generally. This growth on an extremely vascular region of relatively very low follicle population, and very limited area, might be least expected to show such an effect, but rather to maintain, as in fact it does, a much higher sulphur content than wool fibre.

The appearance of medulla, associated with a breakdown in the cystine incorporation, represents the other extreme, and experimental evidence as to the existence or not of intermediate stages is certainly desirable.

#### THE LAWS OF SWELLING.

By J. R. KATZ (AMSTERDAM).

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#### 1. Definition of Swelling.

A solid is said to *swell* when it takes up a liquid, whilst at the same time

(a) it does not lose its apparent (microscopic) homogeneity;

(b) its dimensions are enlarged;

(c) its cohesion is diminished: instead of hard and brittle, it becomes soft and flexible.

Only when all three of these conditions are fulfilled may we say that real "swelling" occurs. This definition is due to the earlier botanists (1860-1880), who first made systematic scientific researches on the subject. At that time swelling seemed clearly distinct from capillary imbibition, such as is shown by a solid having many fine capillary canals, e.g. a piece of brick. Such a solid also takes up liquids, but it is clearly (microscopically) inhomogeneous, its dimensions do not change (it does not swell), and its cohesion is not diminished through imbibition of liquid.

Since this time, through the development of modern colloid chemistry, we have good reason to doubt whether the boundary line between the two phenomena is always as sharp as would be desirable for a clear distinction to be drawn. When the order of magnitude of the capillary tubes is very much too small to be visible under the microscope, but larger than the distance between single molecules, there may exist phenomena lying half way between real swelling and real capillary imbibition. In those cases it is advisable to study the changes of the dimensions and the cohesion of the solid, and to compare them with the amount of liquid taken up by the solid. Up to the present, very little systematic work has been done in this borderland between the two typical phenomena (cf. MacBain's sorption).

## 2. Solids which are Capable of Swelling.

Roentgenspectrography has shown in a large number of cases that solids which can swell are built up of a large number of very minute (submicroscopical) crystals, and that those crystals have a long stretched form (being, for example, five times as long as they are thick; approximately these crystals might be, for example, 10  $\mu\mu$  thick, 50  $\mu\mu$  long) (Mark and Hengstenberg).

Those solids which can swell consist in the great majority of cases of substances of high molecular weight, generally polysaccharides, albuminoids or polymerised substances (e.g. rubber, polystyrol). It has become very probable in recent years that all these substances of high molecular weight are built up from elongated micellæ, and that their molecules have the form of long threads. It therefore seems probable that this form of the micellæ (and the form of the molecules) has some connection with the fact that these solids can swell.

It is, however, difficult to make a complete picture of this connection. According to one possible theory, the long micellæ would form a structure like the fibres in felt. We could thus understand how it is that such bodies can take up liquids and yet not lose their cohesion entirely but only partially. One could assume, again, that the micellæ are connected to one another at certain spots of their surfaces, while other parts of these surfaces would bind the liquid by adsorption. It is possible, however, that the micellæ of swelling bodies have other qualities (not

at present well understood), which must be taken into account.

¹ Vide Nägeli, Reinke, Pfeffer, Hugo de Vries; their well-known textbooks or monographs refer to the literature on the subject. Before these writers, the physicists who tried to construct a good hygrometer studied the subject (Suerman, Ann. Acad. Lugdun. Batav., 1829-1830, Resp. ad questionem physicam, gives a good review about them). Especially Deluc in 1791 made some valuable contributions; but it is only through the work of the above-mentioned botanists that the subject was really started (Deluc, Phil. Trans., 81, 1-42, and 389-421, 1791, an article which is still very interesting).

Moreover, another possibility occurs, namely, that the liquid is not adsorbed, or not only adsorbed, at the surface of the micellæ, but that it penetrates into the interior of the micellæ, forming something like a solid solution. The form of the molecules might then give the explanation of the fact that substances of high molecular weight are almost always swelling bodies; the attraction between the molecule-threads is much weaker than the attraction between the parts of a molecule along the length of the thread, and this might make solid solution more easily possible than in other cases.

We shall see in a later paragraph that it has been possible in some cases to show that probably the swelling is due to adsorption of liquid at the surface of the micellæ, while in other cases it is due to absorption

in the interior of the micellæ.

In recent years a few inorganic substances have been discovered, which show swelling, e.g. silicates. These substances may become important for the theory of the phenomenon as their molecules probably have a different form; the form and properties of their micellæ ought to be compared with the theories described above.

There exist swelling crystals. Since the middle of the nineteenth century albuminoid crystals (vitellins) are known which can swell (and lose water) without ceasing to behave like crystals. They can be extracted from the seeds in which they occur naturally (Ricinus, cucumber, hemp, Bertholletia) by lukewarm salt solutions. When cooling these solutions, the vitellins crystallise in vitro. Hæmoglobin crystals are also capable of swelling. These crystals take up and lose water without any change in their apparent (microscopic) homogeneity.2 In aqueous solutions of many aniline dyes they take up the dye (into their interior and in homogeneous distribution), while the solution in many cases becomes colourless. While crystals as a rule do not take up foreign substances, and are therefore used for preparing substances in a pure condition, these swelling crystals have an extraordinary power of absorbing all sorts of foreign substances. Their crystal angles are often irregular and distinctly different from what they ought to be according to the crystal system; for instance, in the case of hexagonal plates, the angles might deviate up to 5° from the theoretical value of 120°. These deviations may be connected with the softness and fluidity of these crystals in a swollen condition; in a dry condition they are hard and brittle.

Swelling crystals have considerable theoretical interest. If they are really homogeneous, this would prove that at least in these cases swelling is due not to an adsorption of liquid on the surface of micellæ but to something like the formation of a solid solution. However, v. Nägeli (1862) doubted whether they are real crystals. Because they swell and absorb dyes he called them "Scheinkristalle," and believed that they were built up from micellæ which are regularly oriented. Others, including the author, have considered them as real crystals, but as crystals which can swell. The latest developments in crystallography seem to hint at the fact that these two points of view may not be so entirely different as they may seem. Every crystal seems to be built up from units containing approximately 105 molecules.

In recent years many new swelling crystals have been discovered; but our theoretical understanding as to the mechanism of their swelling

<sup>&</sup>lt;sup>2</sup> For swelling crystals: C. v. Nägeli, Sitzungsber. d. Münch. Akad. d. Wiss., 120-154, 1862; Schimper, Diss. Strassburg, 1878; Maillard, Revue génér. d. sciences pures et appliquées, 608-674, 1898.

is insufficiently developed. It may be added that crystals which can swell do not show the X-ray diagram of ordinary crystalline substances.

Loewenstein, working in Tammann's laboratory, discovered that crystals of an inorganic substance, of a certain basic zirconium oxalate, can swell in an analogous way. When these crystals are prepared by the evaporation of a concentrated solution they are hard and brittle and look like ordinary crystals. If, however, they are put into a desiccator filled partly with water they absorb water vapour, swell to the double volume, and acquire a consistency like butter. Unfortunately, it has not been possible to reproduce these crystals; there exist many basic zirconium oxalates, and probably Loewenstein's prescription is not exact enough to prepare the right one. There can be no doubt, I think, that his observations have been correct.

#### 3. The Liquids which cause Swelling.

The classical observations were all made with water or aqueous solutions as the liquid absorbed in the swelling body. Certain solids, however, such as rubber and esters of cellulose, swell in a large number of organic liquids.

The swelling in water and in alcohol—liquids which "associate," containing complex molecules—is probably a more complicated phenomenon than the swelling in organic liquids which are not associated (like, for instance, benzene or hexane). For it is probable that during the swelling the state of association of an associating liquid is changed.

## 4. Distinction between the Primary Phenomenon and Secondary Complications.

The earlier observations on swelling were made without sufficiently clearly making this distinction. It is not right to investigate the phenomenon of swelling by the use of such highly organised bodies as peas or stems of Laminaria; they are built up out of parts having very different properties and constitution. It is necessary to choose substances for the investigation of the laws of swelling which are as simple and uncomplicated as possible. The "chemically pure" polysaccharides and albuminoids approach this requirement as much as possible. In the same way natural fibres and natural starch granules are too complicated, as they contain a complicated and unknown structure.

Moreover, one must avoid the complication of hysteresis as far as possible. All solids show hysteresis, practically in every property investigated. If one changes, for example, the weight pulling a thread, the thread will lengthen to a certain extent. If the weight is then taken away, the former value of the length of the thread will not return, but the thread will remain lengthened.

Similarly, if one brings a substance which is capable of swelling into a water vapour of a given high vapour tension (all at the same temperature), it will take up a certain amount of water. If, then, it is brought back in water vapour of a lower tension, it gives off less water than it formerly took up. The phenomenon therefore is not reversible; it is complicated by hysteresis. If we bring the substance into water vapour of different values, and wait each time until approximate equilibrium is

E. Loewenstein, Z. anorg. Chem., 63, 117, 1909.
 J. R. Katz, "Gesetze der Quellung," Koll. Beih., 9, 1, 1917.

reached, we shall get a different curve when going in the direction of increasing vapour pressure than when going in the direction of diminish-

ing vapour pressure.

If we want to study the phenomenon in its simplest form, however, what we must aim at is the equilibrium curve (each point of which is a state of real equilibrium). This is only approximately possible. In studying the properties of a solid, one can try to avoid this difficulty in one of the three following ways, which can all be applied to the study of swelling. As a first approximation, one can simply neglect the hysteresis, taking the line of approximate states of equilibrium (when going in one of the two directions) as the real line of equilibrium. Or, as a better approximation, one can determine the two lines, going in both directions, and construct a line lying half way between these two. This way has been chiefly used in studying swelling.5 It would probably be still better to make the vapour pressure alternate very slowly between two limits; then the amount of water absorbed will gradually approach a limit, a so-called natural state, which is equivalent with a real state of equilibrium. This third way has not yet been applied to the study of swelling; but in studying other properties of solids it has proved useful, although elaborate.

## 5. The Maximum of Swelling (Quellungsmaximum).

When a swelling substance is put into pure water it may reach a state in which no further water is taken up. This limit is called the maximum of swelling, and substances showing such a maximum are called substances with limited swelling (begrenzte Quellung). Most swelling substances are of this kind. Others, such as gum arabic or ovalbumine, do not reach a limit in swelling, and gradually swelling changes into solution. Such swelling is called unlimited swelling.

Formerly (1880) it was thought that this distinction was a sharp one. But in later years it has proved to be sometimes indefinite: there sometimes exist cases where it is difficult to distinguish to which of the two

groups a swelling substance belongs.

In colloid chemistry and applied colloid chemistry it is often necessary to determine the water content at the maximum of swelling. For this number is a simple aspect of the tendency to swell (although not the only one). In doing so, it must be remembered that this maximum can only be correctly determined by immersing the swelling body into liquid water; saturated water vapour will not do. This fact was first noted by Deluc in 1791, while experimenting with his whalebone-hygrometer. It was later observed by von Schroeder (1903) and is sometimes called the von Schroeder effect; this however is not correct, it ought to be called the Deluc effect.

Deluc and von Schroeder both observed that in "saturated" vapour a swelling body (whalebone, gelatine) will reach a different state of apparent equilibrium (absorbing less, often very much less water) than when immersed into liquid water. Deluc explained this difference by proving that the so-called "saturated" vapour was not really saturated; and that the difference disappeared if the vapour was really saturated. Later experiments of Wolff and Büchner seem to show that this is the

<sup>&</sup>lt;sup>5</sup> J. R. Katz, *loc. cit.*; *Ergebn. d. exalt. Naturw.*, **3**, 340-342, 1924; see also under paragraph 9 of the present article.

under paragraph 9 of the present article.

6 Deluc, Phil. Trans., 81, 1-42 and 389-421, 1791.

7 P. von Schröder, Z. physik. Chemie, 45, 76, 1903.

correct explanation.<sup>8</sup> But there remains some doubt, and the question is still an open one.<sup>9</sup> In swelling in other liquids than water similar phenomena have been observed.

Another difficulty in determining the maximum of swelling occurs in the many cases where the swelling body has no simple form. If it is, for instance, a thin plate or a sphere, after swelling it can be well separated from the liquid by drying it off with Joseph paper (or some material like this) and weighing it; then determining the water content in the maximum of swelling is a simple thing. But if the swelling body has the form of a fine powder, it will prove impossible to separate it from all capillary adhering water by pressing it off, without at the same time pressing out a certain amount of swelling water. It then is impracticable to determine directly and exactly the amount of swelling water.

One then is forced to use an indirect method which may show that in one case there is more swelling in the maximum of swelling than in the other case (without determining the exact numbers). Very often it is then found useful to decant the pulverised substance in measuring glasses, or to centrifugate it, taking the volume of the decantate or centrifugate as a measure of the degree of swelling. Or if the powder is fine and equal one may determine the viscosity of the mixture, which will be found the greater—at the same concentration—the greater the degree of swelling. If the substance does not have the form of a fine and homogeneous powder one may try to bring it into this form by some standard process. Many important phenomena can only be investigated with some indirect method of this kind.

## 6. Difficulties in Eliminating the Last Amounts of Liquid from a Swollen Substance.

It is a well-known fact that it is very difficult to eliminate the last traces of water from a substance swollen in water. If one applies vacuum at room temperature, an apparent equilibrium is reached. If, however, we then dry at a higher temperature more water is given off, the more so the higher the temperature. But soon, in increasing the degree of heat, the substance begins to turn yellow or to give other signs of decomposition. In most cases it has proved useful to dry in a vacuum over  $P_2O_5$  at 100°; but it is not quite certain that this eliminates all the water. In other cases drying at 110° or 120° in a current of dry nitrogen or hydrogen has been used, but the result is no more certain.

In the same way it proves very difficult, almost impossible, to eliminate the last amounts of acetone or other organic liquids which have been used for preparing films of acetylcellulose. Several per cents. of the liquid may prove so firmly bound that they are not eliminated by a long drying.

It therefore is more or less arbitrary, what is to be considered as a "water free" swelling substance—in making quantitative investigations about the laws of swelling in water. It is advisable to take as such a substance dried at  $100^{\circ}$  in vacuo over  $P_{\circ}O_{\circ}$ .

It is a general experience that when a swollen body has been fully dried, it never afterwards takes up so much water as it contained before drying. This holds particularly strongly for organised substances,

<sup>&</sup>lt;sup>8</sup> L. K. Wolff und E. H. Büchner, Z. physik. Chem., 39, 271-280, 1915.

<sup>9</sup> An excellent review of the present state of the question is given by H. Freundlich, Kapillarchemie, II (latest edition), p. 567 and 611, 1932.

animal or vegetable tissues, but is a general experience in working with swollen substances, and often explains practical or technical difficulties in working with such substances. It is allied to hysteresis, but may have partially a different explanation. It recalls similar experiences in the solubility of polysaccharides and albuminoids. For instance, the polysaccharide lichenine, when not yet dried, is easily soluble in warm water, but is nearly insoluble when dried in the air; if however it is dried with absolute alcohol and ether, it remains soluble in hot water (P. Karrer).

## 7. Intermicellar and Intramicellar Swelling; Permutoid Form of Swelling.

The first primordial question in understanding swelling is to know whether the liquid penetrates into the interior of the micellæ or is only adsorbed at their surface. X-ray spectrography can—as the author

showed in 1924—answer this question to a large extent.10

When we find that the X-ray diagram is different before and after swelling, we can be pretty sure that liquid has been taken up into the interior of the micellæ. If the liquid is only adsorbed at the surface of the micellæ we should find no change in the X-ray diagram (surface layers giving no X-ray diagram of their own, because they are too thin; at most the amorphous diagram of the liquid can appear super-imposed over the diagram of the solid). But we are not entitled to draw from the unchanged diagram the conclusion that liquid did not penetrate into the interior of the micellæ: if only one or two layers of molecules are attacked by the liquid, there may be no change in the X-ray diagram (as there is no new period of identity formed); moreover, if in the swelling substance there should be some intermicellar substance, working like lime between the bricks of a building, this intermicellar substance might be changed without influencing the X-ray diagram, because its amount is too small.

In the case when the X-ray diagram is changed, we may distinguish two cases:—

- (a) The dimensions of the elementary cell of the crystals are enlarged according to a continuous function of the degree of swelling; then we call it intramicellar swelling; when the change in the dimensions of the elementary cell is so large as to explain almost the whole change of the dimensions in the swelling body, we may say that this swelling is chiefly intramicellar. It has then very much the character of the formation of a solid solution of water in the solid, as van't Hoff would have called it. This is the case with gelatine and collagen and with graphitic acid.
- (b) There is a marked change in the X-ray diagram; this change is not a continuous function of the degree of swelling, but a new diagram is formed, while the old loses in intensity. In this case we must assume that the liquid forms a chemical compound with the solid, and that each crystal of the solid is changed by pseudomorphosis into a crystal of the compound. In this case the swelling is in no way explained by the

<sup>&</sup>lt;sup>10</sup> J. R. Katz, Physik. Z., 25, 351, 1924; Ergebn. d. exalt. Naturw., 3, 348-372, 1924; in Kurt Hess, Chemie d. Zellulose, Akad. Verlagsges, Leipzig, 1927; Micellartheorie und Quellung der Zellulose, p. 605-769. See also Carl Trogus and Kurt Hess, Z. physik. Chem., (B)5, 161, 1929, and (B)7, 1, 1930; Carl Trogus, Kurt Hess and J. R. Katz, Ibid., (B)7, 17, 1930; K. Hermann, O. Gerngross and W. Abitz, Ibid., (B)10, 371, 1930; J. R. Katz and J. C. Derksen, Rec. trav. Chim. Psys.-Bas, 50, 149, 248, 746; 51, 513, 1931, etc.

change of the X-ray diagram; for the explanation of the swelling another mechanism must be taken into account, viz., the adsorption of liquid on the surface of the micellæ. The permutoid change of the crystal structure of the solid is, so to say, an accessory phenomenon in the mechanism of swelling. In this case we speak of permutoid swelling. This case is realised in the swelling of trinitrocellulose in camphor, in cyclohexanon, in acetone and in other solvents of nitrocellulose. Perhaps the compound binds more liquid than the substance does before.

In the case of permutoid swelling, we often find that the system reaches a final state, which seems to possess one degree of freedom more than the phase-rule would allow. We find—out of the X-ray diagram —that the number of crystals changed in their inner structure is—within certain limits of concentration—the greater as the concentration of the swelling liquid is greater. Evidently the case we are studying is more complicated than the cases covered by the ordinary phase rule of Gibbs. There must be one force influencing the equilibrium, which is not taken into account in applying the ordinary form of the phase rule. Or, the crystals must all be in different conditions. This force is evidently given by the arrangement and interaction of the micellæ. In this way we must explain, for instance, the fact that when cellulose fibres swell in concentrated solutions of sodium hydroxide, the amount of cellulose changed into natroncellulose is the greater the more concentrated the solution. One may assume that the force mentioned above is different in strength for each little heap of micellæ in a cellulose fibre, therefore giving an amount of crystals permutoidically changed, according to a Galton-Quetelet curve of probability (as a function of the concentration).

(c) The X-ray diagram is not changed through the swelling. In this case—with the exception mentioned before—we may conclude that there is no change in the interior of the micellæ, only at their surface, where layers of liquid are adsorbed according to the laws of surface adsorption. In this case, we may call the swelling an *inter*-micellar one.

I think it important to clearly distinguish between these three forms of swelling, as they must be different phenomena, though all covered by the same name and by the same definition.

So far as I can see, X-ray spectrography is for the time being the only experimental method which allows us to penetrate into the intimate mechanism of swelling.

## 8. Is there some Connecting Material which Unites the Micellæ of a Swelling Substance?

When one precipitates bariumsulphate or arsenious trisulphide, no swelling substance is formed, there is no cohesion between the micellæ of the precipitate; when dried it is easily pulverised. On the contrary, if we precipitate cellulose from one of its solutions a swelling substance is formed, which has a very strong cohesion between its micellæ; when airdried it is extremely difficult to pulverise it. What makes the difference between the two cases?

We have seen, in section 2, that the long-stretched form of the micellæ may be the underlying cause of the difference. But the possibility occurs that there may be another cause. There might be a binding substance in a swelling substance which binds packages of micellæ together to larger, but probably still submicroscopical, units. In grown products, tissues, fibres, starch granules, this binding substance

might take the form of membranes lying between the micellæ or between small bundles of micellæ. A good example of such a structure—but a hundred times larger, therefore microscopically visible—is given by breadcrumb. In the dough the starch granules are united by the gluten which in the wet state is elastic and plastic at the same time. In the baking process this gluten is coagulated. If now we examine thin slices of the breadcrumb, we find the starch granules-swollen through a beginning of gelatination—surrounded by a network of coagulated gluten which surrounds every starch granule (or sometimes every two or three of them), and now works between the starch granules like lime between the bricks of a wall.

Kurt Hess and his pupils have pointed out that a structure of the same kind-but in much smaller dimensions-might exist in cellulose fibres and gave some evidence for supporting this theory. For instance, the well-known fact that fibrous substances shorten when swelling strongly—which it is so difficult to explain—is, according to them, explained by the working of membranes of a foreign substance lying between the cellulose micellæ of the fibre. 11 The author has brought some evidence that a structure of this kind may exist in starch granules and may play an important rôle in the gelatination of starch (explaining facts which otherwise it would be difficult to explain). Both fibres and starch granules, however, are plant products, with all the complications of a product of living matter.

Even if these assumptions should be binding for fibres and for starch granules, this would not imply that in chemically pure swelling substances, precipitated in vitro, there would be such a binding substance between the micellæ. Although it is possible, we do not have sufficient reasons to believe it. In every case it would be very much exaggerated to assume that there is no swelling possible without such a binding substance.

### Vapour Pressure (Free Energy) and Heat of Swelling; Thermodynamics of Swelling.

We may hope to get an important insight into the mechanism of swelling by measuring the free energy of swelling (which is a measure of the affinity of the liquid for the solid) as a function of the degree of imbibition. It will then be worth while to compare this energy with the heat of swelling (measured also as a function of the degree of swelling). With this object, the author published (1910-17) extensive researches upon the affinity for water of a number of polysaccharides and albuminoids. 12 At his instigation, A. Hofmann (in 1924), 13 and J. C. Derksen (at present) continued these researches for the case of swelling in organic liquids.

Free energy of swelling is most easily determined from the vapour pressure of the liquid in a partially swollen substance. If A is the decrease of free energy, when a partially swollen substance in the state I

<sup>&</sup>lt;sup>11</sup> Membranes are partially arranged in a different and more complicated form

in order to explain this shortening (Kurt Hess, Lüdke).

12 J. R. Katz, loc. cit. and Ergebn. exakt. Naturw., 3, 372, 1924.

13 Alfred Hofmann, Ueber die Quellung von Zellulosederivaten und Kautschuk in organischen Flüssigkeiten, Diss., Berlin, 1925 (existing only in typewritten copies, available in University-library, Berlin); extensive quotations, Ergebn. exakt. Naturw., 4, 200-8. 1925.

takes up one further gram of water (while the quantity of swollen substance is so large that its degree of swelling is not changed), we have the thermodynamical formula:

$$A = -RT \log h_1,$$

where  $h_1$  is the vapour pressure as a fraction of the maximum pressure of water at the same temperature, R the gas constant for I gm. water, and T the absolute temperature. For room temperature the formula gets the form:

$$A = -\frac{1252}{18} \log h_1,$$

from which A can be easily calculated, if we have measured  $h_1$ .

Unhappily, the vapour pressure has a strong hysteresis. By  $h_1$  we mean the state of real equilibrium which is best approximately found by measuring  $h_1$  from the two sides (after drying and after wetting) and taking the average of the two values.

For measuring the vapour pressure as a function of the degree of swelling in a large number of cases, the author found van Bemmelen's method most adequate. Some more recent observations by different authors, contradicted by others, seem to show that in a very high vacuum, which has eliminated the last traces of air from the interior of the solid,

hysteresis may entirely disappear.

For every determination of a vapour pressure two samples of airdry substance are weighed off. One is dried at room temperature in a vacuum exsiccator over strong sulphuric acid; one is wetted in an exsiccator over water. Both are then put in an exsiccator with a mixture of water and sulphuric acid having a known vapour pressure. When the two samples have acquired a constant weight, the average of their water content gives the degree of swelling which is in equilibrium with the vapour pressure.

Substances such as casein, nuclein, serumalbumin, and gum arabic all give vapour pressure curves of the same S-shape, which is character-

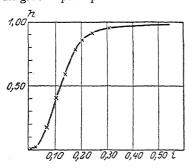


Fig. 1.—Casein.

istic for the swelling in water (Fig. 1). The degree of swelling is expressed as gms. of water per gm. of dry substance.

Fig. 2 shows the form of the curve, according to which the decrease of free energy follows the degree of imbibition.

If one determines the vapour pressure of swelling crystals (CO-hæmoglobin or vitellin, for example), one finds curves of exactly the same form as for substances which apparently are amorphous.

The heat of swelling is strongly positive in all cases investigated. We must distinguish two kinds of heat of swelling. The integral heat of swelling (W) is the amount of heat developed when I gm. of dry substance takes up i gms. of water; this quantity was measured in a thermometric calorimeter. The differential heat of swelling (w) is the

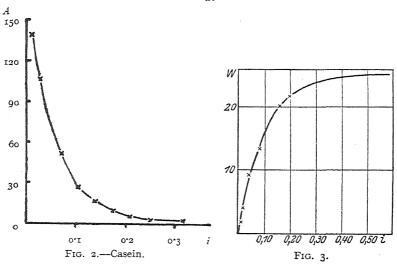
J. R. KATZ

TABLE I.-CASEIN.

i.	h.	$-\frac{1252}{18}\log h \text{ (in Cal.)}.$
0.	0.	}
0.011	0.010	139
0.029	0.022	115
0.070	0.176	52.5
0.106	0.410	26.9
0.140	0.596	15.7
o•18o	0.788	7.2
0.207	0.853	4.6
0.245	0.914	2.7
0.319	0.962	1.2
± I.0	1.000	0

amount of heat developed when a very great amount of partially swollen substance (water content i) takes up I gm. of water. We may state

$$w = \frac{dW}{di}$$
.



w was calculated from the Wi curves. It is difficult to determine W with exactitude, as swelling is a process the last degrees of which are very slow. This makes  $\frac{dW}{di}$  decidedly uncertain. There may be a constant systematic error in the values found for  $\frac{dW}{di}$ . W depends on i according to a curve which is approximately a hyperbola:

$$W = \frac{Ai}{B+i},$$

where A and B are constants, different for each swelling substance. Fig. 3 (Table II.) gives the curve for casein:

TABLE II.

i.	W (in Cal.).			
0.	0·			
0.021	4·2			
0.042	9·2			
0.081	13·4			
0.154	20·1			
0.196	21·7			

The so-called *initial heat of swelling*, the amount of heat developed when a very large amount of completely dry substance takes up I gm. of water, is very large. For  $[w]_{i=0}$  a value of 250 to 420 cal. was found:

Casein.		•					265	cal.
Nuclein	•		•		•		310	,,
Cellulose			•	•	•		390	,,
Inulin	•						420	,,
Artif. starch	corns						315	,,

For swelling crystals, e.g. edestin, a value of about 200 cal. was found, therefore, of the same order of magnitude. These numbers and curves serve to measure the forces which bind the water to the solid. These forces are very great for the first amount of water, they rapidly decrease with the amount taken up; for strongly swollen substances they are very small. It will be very difficult to read from these numbers and curves whether the swelling in a given case is intermicellar, intramicellar or permutoid; guided only by the X-ray diagrams, we may try to use them for solving questions of this kind.

In the case of swelling in organic liquids analogous results were obtained (nitrocellulose, acetylcellulose). But there are two differences—which, as we shall see later, are probably connected: the initial heat of swelling is smaller, amounting only to 60 to 110 cal. and the S-shape of the vapour pressure curve is less evident or is lacking; in this case the vapour pressure curve turns its concave side to the *i*-axis from the very beginning. Evidently the forces which bind the organic liquid to the swelling solid are weaker than in the case of water. The curves of the free energy and of the heat of swelling show a great similarity, however, with those in the case of water.

Considerable insight into the mechanism of swelling is gained if we compare the decrease of the free energy and the differential heat of swelling. In a condensed system like this the difference between free energy and differential heat of swelling is given by  $T\eta$ , where  $\eta$  is the change in entropy when I gm. of water is taken up by a very large amount of partially swollen substance (water content i), and where T is the absolute temperature. If  $\eta$  were approximately zero, the swelling would be entirely the consequence of the attractive forces between solid and liquid. If  $\eta$  has an important value, something more is happening in the process of swelling: a change in the probability of the distribution and arrangements of the water molecules.

It is difficult to measure the differential heat of swelling so accurately that the change in entropy can be well determined; the more so because the decrease in free energy is made uncertain by the hysteresis in the vapour pressures. In the determination of the differential heat of swelling there might be a constant error. Because of these causes of

error the author compared, in 1917, only the "changes" in the free energy and in the differential heat of swelling, and found that these changes were approximately equal for small degrees of imbibition. One may therefore try to neglect the differences found between the absolute values of the decrease of free energy and the differential heat of swelling, and assume as a first approximation that they are due to experimental errors.

Fricke and Lüke <sup>15</sup> reverted to this question in 1930. They determined the differential heat of swelling in two independent ways: from the integral heat of swelling and from the changes of the vapour pressure with the temperature (from a formula analogous to the Kirchhof formula for liquid mixtures). As these two quantities agreed rather well, and as experimental errors are of a very different character in both cases, Fricke and Lüke considered their values for the differential heat of imbibition as sufficiently certain to compare them with the values of the free energy. They form important differences. In every case there was an important decrease in entropy through the swelling. An explanation for this decrease

of entropy was not given.

The author considers this new experimental evidence as sufficiently There evidently exists a decrease in entropy through the swelling. For small degrees of imbibition this decrease of entropy is often approximately independent of the degree of swelling. How can this decrease of entropy be explained? Evidently by the development of a less irregular arrangement of the molecules of the water than in the case of liquid water; they must be lying less at random. As a similar decrease of entropy is found in the case of the formation of salt hydrates, and as the amount of decrease in this case is of the same order of magnitude as in the case of swelling, there may be two possible explanations. Either the degree of association of the water is changed through the swelling; or some regular arrangement, as in the formation of crystals, occurs in the water which is taken up in the swollen solid. One may hope to decide between these two possibilities by making analogous experiments with the swelling in organic non-associating liquids, where the first of the two factors can be excluded. Research work of this kind is being made at this moment in the author's laboratory by J. C. Derksen.

If as a first approximation  $\eta$  is considered independent of i, the form of the vapour pressure curve will be connected with the value of the differential heat of swelling  $[w]_{i=0}$ . The greater  $[w]_{i=0}$ , the stronger the S-form of the vapour pressure curve. The calculations formerly made by the author (1917) under the assumption  $\eta=0$ , remain valuable for the greater part when  $\eta$  is approximately independent of i.

A few words may be added about the *pressure of swelling* and its thermodynamical relation to the vapour pressure of the partially swollen substance. This relation is (approximately)

$$P = -\frac{RT}{MV_0} \ln h.$$

P is expressed in atmospheres, M is the molecular weight,  $V_0$  the specific volume of the liquid, h the reduced vapour pressure.

The form of the Pi curve—calculated from the vapour pressure curve—is therefore analogous to the curve of the free energy (Fig. 2). For small degrees of swelling, when h is very small, P amounts to thousands

<sup>15</sup> Fricke and Lüke, Naturw., 18, 307, 1930; Z. Elektroch., 36, 309, 1930.

of atmospheres. That the swelling pressure may be very large was known already in antiquity. The Egyptians, for example, when isolating stones from the rocks, filled a hole in the rock with very carefully dried wood, and then poured water over it. The force developed by the swelling wood made the stone burst.

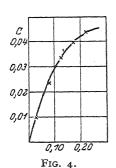
Experimental determinations of the swelling pressure have been made by Reinke, Freundlich and Posnjak, v. Terzaghi, Stamberger and Blow.16

V. Terzaghi and Hill 17 found the remarkable fact, that the direct measurements of the swelling pressure do not agree with the values calculated from the vapour pressures. This seems to be in contradiction with the second law of thermodynamics. Stamberger, 18 however, found coincident values, when measuring the vapour pressure and the swelling pressure of rubber, partially swollen in benzene or chloroform. Freundlich 19 explains the results of v. Terzaghi and Hill by the fact that in both cases not exactly the same quantity is measured. In measuring the vapour pressure, only the volatile liquid will go through the boundary between gel and liquid, while in the case of swelling pressure non-volatile substances dissolved in the volatile liquid will go through too. This interesting phenomenon would deserve a more explicit study.

It may be added that from a thermodynamical point of view swelling pressure and osmotic pressure are very much the same thing. In both cases the pressure is the consequence of the fact that one component of the system can move throughout the whole system, while the other component must remain within a limited part of it. From a thermodynamical point of view it is unimportant whether this is realised with the help of a semipermeable membrane or without it.

### 10. Heat of Inbibition and Volume Contraction.

When a solid swells in water there is always a marked decrease in the total volume of the system; the volume of a swollen body is smaller



This volume contraction—measured in cm.3 pro I gm. of dry solid-depends on the degree of swelling i according to a hyperbola,

$$C = \frac{fi}{g+i}$$

Fig. 4 shows the volume contraction of casein in relationship with i.

than the sum of the volumes of solid and liquid.

This hyperbola recalls closely the hyperbola of the (integral) heat of imbibition. The analogy was then studied more closely. It seemed rational that the volume contraction would be-as the heat of swelling—an expression of the attractive

forces between liquid and solid. There was, however, no strict proportionality between volume contraction and heat of imbibition for different degrees of swelling of a same substance; the ratio of the two may change in the proportion of one to two. But it became clear in comparing

<sup>16</sup> H. Freundlich, Kapillarchemie, 3rd edition, II., pp. 569 sqq.
17 v. Terzaghi and Hill, Colloid Sympos. Monogr., 4, 58, 1926; Handb. d. physik. und techn. Mechanik. IV., 2. Hälfte, 568 sqq., 1931.

18 J. Stamberger, J. Chem. Soc., London, 1929, p. 2318.

19 H. Freundlich, loc. cit., p. 575.

different swelling solids—all swelling in water—that the ratio between volume contraction and heat of imbibition is always of the same order of magnitude: from 10  $\times$  10<sup>-4</sup> to 30  $\times$  10<sup>-4</sup> (c expressed in cm.<sup>3</sup>, W in cal.,  $\frac{c}{W}$  taken for i=0):

Casein							$15 \times 10^{-4}$ .
Nuclein							$30 \times 10^{-4}$ .
Inulin					•		$28 \times 10^{-4}$ .
Artificial	starc	h cor	ns			-	$II \times IO^{-4}$ .
Edestin c	rysta	ls					$14 \times 10^{-4}$ .

It may be remarked that the volume contraction for the initial amounts of water absorbed by a dry swelling body is remarkably large; it was found for  $\left(\frac{dC}{di}\right)_{i=0}$ :

The first absorbed water therefore has a specific volume of only 0.7 to 0.6. This may be the expression of a very strong attraction between solid and liquid; but it may also be due to a change in the degree of association of the water.

## The Change in the Mechanical Properties of the Solid through Swelling.

It is a well-known fact that all swelling bodies are harder and more brittle when dry than when wet; when wet they are elastic and soft. Bread crust and lichens are examples which everyone knows. Gelatin is a particularly good example. If one wants to pulverize it, it must be sharply dried; when it contains several hundred per cents. of water it is elastic like rubber. This change in cohesion has not yet been so thoroughly studied as would seem desirable.

The modulus of elasticity is greatly diminished by swelling. In studying these changes in a quantitative way, it is necessary to distinguish elasticity and fluidity, especially in the case of strongly swollen substances. Clerk Maxwell <sup>20</sup> gave in 1868 a formula for the deformations of substances which have both elasticity and fluidity. This formula may be helpful in distinguishing the two in the case of strongly swollen substances. If S is the deformation, F the deforming force, then the force F will give at the same time an elastic deformation proportional to  $F\left(\frac{1}{E}F, \text{ where } E \text{ is the modulus of elasticity}\right)$ , and a fluidity change  $\frac{dS}{dt}$ , which will be

proportional to  $F\left(\frac{\mathbf{I}}{\sigma}F$ , where  $\sigma$  is the coefficient of viscosity). According to Maxwell, we may write,

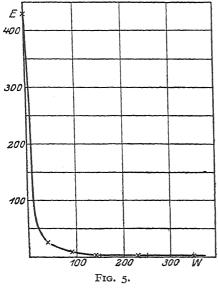
$$\frac{dS}{dt} = \frac{I}{E} \frac{dF}{dt} + \frac{I}{\sigma} F.$$

When  $\sigma$  is small, then we have the case of a liquid; when  $\sigma$  is great, then we have the case of a solid. In dry substances  $\sigma$  is very great, in

<sup>&</sup>lt;sup>20</sup> Clerk Maxwell, Phil. Mag. (XIV), 35, 134, 1868.

swollen substances it is often much smaller. In such cases the phenomena are very complicated.

If we can free the elastic phenomena approximately from the pheno-



mena of fluidity, we find that the modulus of elasticity as a function of the degree of swelling i first diminishes very rapidly, then more slowly, and that it gets very small values for great values of i. for great values of i. Fig. 5 shows the change of E for pieces of laminaria; (J. Reinke, 1879).

This change of the modulus of elasticity through swelling is better understood,21 if we compare the change in the constant  $\mu$  of Poisson. For most solids (swelling bodies in a dry state inclusively) the value of  $\mu$  lies between 0.2 and 0.5. In general,  $\mu$  is the smaller, the harder the substance is. When the substance is only half solid  $\mu$  is almost exactly 0.500.

Steel					0.269
Glass					0.245
Copper					0.329
Lead					0.400
Ebonite					0.389
Rubber					0.490
Paraffin					0.500
Gelatin :	gel				0.200

It is therefore probable that  $\mu$  increases with the degree of swelling i, and that for large degrees of swelling  $\mu$  has a value very near 0.500.

Now, the well-known formula connecting E and  $\mu$  is:

$$E = \frac{3(1-2\mu)}{K}$$

where K is the coefficient of cubic compressibility.

If  $\mu$  approaches 0.500, then E must get very small values. This is just what the experiment has shown (Fig. 5).

### 12. The Analogy between Swelling and Solution as a Heuristic Principle.

Swelling is in many ways analogous to solution. Where the micellæ are of submicroscopical size it will-even in the case of pure intermicellar swelling—be a good approximation of the real situation, if we compare swelling with the formation of a solution (of water in the solid).

The author has shown 22 that the quantitative laws of swelling, described in paragraphs 9 and 10 may all be understood from this principle. Liquids such as sulphuric acid and phosphoric acid, which are only very slightly volatile, which mix easily with water, and which

<sup>&</sup>lt;sup>21</sup> Gesetze der Quellung, Koll. Beih., 9, 150, 1917. <sup>22</sup> Gesetze der Quellung, Koll. Beih., 9, 118-146, 1917.

give a strong development of heat when mixed with water, show curves for the dependancy of water vapour pressure, heat of mixing and volume contraction very analogous to the laws of swelling described before.

Even the relation  $\left(\frac{c}{\overline{W}}\right)_{i=0}$  is of the same order of magnitude as in the case of swelling substances:

(swelling substances from  $10 \times 10^{-4}$  to  $30 \times 10^{-4}$ ).

It is possible to deduce all the characteristics of the quantitative laws of swelling from the theory of binary mixtures of van der Waals, on the assumption that the molecular weight of the one component is many times as great as that of the other component.<sup>23</sup> Then, according to van der Waals' formula for b there must be a very strong volume contraction. This will lead to a strongly positive development of heat, and this to an

S-shape of the vapour pressure curve. Even the fact that  $\left(\frac{c}{W}\right)_{i=0}$  has approximately the same value in different substances can be predicted from the theory; it is parallel to the well-known fact that the critical pressure is not very different for different substances.

In many other cases the analogy between swelling and solution will probably prove likewise useful in the study of phenomena of swelling.

## 13. Swelling in Aqueous Solutions of Electrolytes; Lyotropic Series.

Complicated phenomena are observed in the case of swelling in aqueous solutions of electrolytes. Wo. Pauli 24 first showed that these phenomena may be explained electrically by the theory that one of the two ions is more strongly absorbed by the micellæ (on their surface only or in their interior also) than the other ion. This conception has become more and more probable. One can then explain the strong swelling in such aqueous solutions (much stronger than in water) in two different ways. One may either accept with Pauli, that the absorbed ion (and the oppositely laden ion immobilised by it) brings its sphere of water with it, and that it is the spheres of water of the ions which give the strong swelling (ions binding more water than micellæ).25 Or, one can explain the strong swelling through the fact that the micellæ, all laden with the same kind of electricity, are repelled from one another by electrostatic forces, and that something like a sponge is formed, in which the water enters so to say passively.26 The first of the two theories seems the more probable; but the other one must be discussed too.

In both cases we can understand the paradoxical fact that those ions give the *strongest swelling* which bind the *smallest* amounts of water, by considering the fact that the interior of the solution and the surface of the micellæ fight, so to speak, for the ions. Therefore, the less water

<sup>&</sup>lt;sup>23</sup> Ph. Kohnstann, Litt. Versl. Kon. Acad. v. Wetensch. Amsterdam, 21, 65-82, 1912.

 <sup>1912.
 &</sup>lt;sup>24</sup> Wo. Pauli and H. Handovsky, *Bioch. Z.*, 18, 340, 1909; 24, 239, 1910;
 Pauli and Valkó. *Elektrochemie d. Kolloide*, pp. 429 sqq.

Pauli and Valkó, Elektrochemie d. Kolloide, pp. 429 sqq.

28 One may compare, for an explicit treatment of this theory, the author's article on Micellartheorie und Quellung der Zellulose in Kurt Hess, Chemie der Zellulose, Akadem. Verlasses. pp. 687-760, 1027.

Akadem. Verlagsges, pp. 687-769, 1927.

26 See also H. R. Procter, J. Chem. Soc., 105, 313, 1914; H. R. Procter and J. A. Wilson, ibid., 109, 307, 1916; J. A. Wilson and W. H. Wilson, J. Amer. Chem. Soc., 40, 886, 1918. The application of the Donnan equilibrium for explaining the hydration (the swelling) must be more closely examined before we can accept it.

they bind, the easier they will be adsorbed from concentrated aqueous solutions on the surface of the micellæ; and therefore the stronger will be the swelling they give. In this way we understand why rhodanides and iodides are very strong swelling agents, while just these ions bind little water. In determining the amounts of salt absorbed by swelling bodies one finds accordingly that this amount increases with the intensity of the swelling (Hofmeister series):

$$CNS > I > Br > Cl > \frac{SO_4}{2},$$

the well-known *lyotropic* series, which—read from the left to the right—gives at the same time the increase of the amount of water bound by the ion.

This very simple explanation of the phenomena may be found helpful in understanding them. It must be remembered, however, that it probably is somewhat too simple. The phenomena of swelling in concentrated aqueous solutions of electrolytes may be very complicated phenomena.

In all these cases of swelling X-ray spectrography is able to distinguish intermicellar swelling and permutoid swelling. Compounds are formed, for instance, when cellulose swells in NaOH, in HNO<sub>3</sub> or in LiCNS solutions.

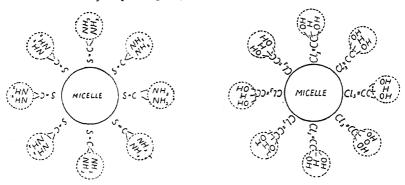
## 14. Swelling in Aqueous Solutions of Organic Substances.

It is a well-known fact that many organic substances which seem rather inactive—such as thioureum, chloralhydrate, resorcinol, benzene-sulphonates give in concentrated aqueous solutions analogous strong swelling of polysaccharides and albuminoids as rhodanides and iodides. The author made, on H. Freundlich's advice, an explicit study of these organic substances, the results of which are published here for the first time.

All substances which contain non-oxidised sulphur in organic binding give in aqueous solutions a strong swelling; thioureum is only a special case. The analogous oxygen compounds work very much less strongly than the sulphur compounds. The swelling effect can be explained by a strong adsorption of the sulphur compound on the surface of the micellæ, the hydrophilic groups of the sulphur compound (e.g., NH<sub>2</sub> in the case of thioureum) binding spheres of water, and therefore making the surface of the micellæ more hydrophilic. That sulphur compounds work much more strongly than oxygen compounds is probably due to the residual valencies of the oxygen atoms in the surface of the micellæ, which bind the sulphur of the organic molecule and therefore further the adsorption.

In the same way, all organic substances which contain halogens in organic binding give strong swelling. In comparing series like acetate, monochloracetate, dichloracetate and trichloracetate, one finds the swelling and the adsorption the stronger the more halogen atoms the organic molecule contains. In comparing different halogens, iodine compounds are found to work more strongly than bromine derivatives, and bromine compounds more strongly than chlorine derivatives. Here again the residual valencies of the oxygen atoms in the surface of the micellæ probably bind the halogen atoms of the organic compound. The water is bound by the hydrophilic groups of the organic compound.

In the case of phenol and resorcinol, the OH groups are probably bound by the surface of the micellæ. While in the case of benzene sulphonate the non-hydrophilic benzene group is probably turned towards the surface of the micellæ; the SO<sub>3</sub> group is turned towards the liquid, and acts as the hydrophilic group.



In this way we may give a simple explanation of the curious fact that aqueous solution of propyl and of butyl alcohol give a much stronger swelling of gelatin and casein than pure water; while these solids do not swell at all in the pure, water-free alcohols. The alcohols are adsorbed on the surface of the micellæ, turning probably the hydrophilic OH group to the waterside and increasing by this adsorption the water-binding capacity of the albuminoid micellæ. If there is, however, not enough water present, this effect cannot develop. Then the dehydrating effect of the alcohols prevails.

In all these cases the adsorption may not only lead to stronger swelling through the presence of hydrophilic groups; it may also work through separating the micellæ from one another (the water entering, so to speak, passively between them). Certain facts seem to indicate that this second theory must be seriously considered, for instance, the strong swelling influence sometimes observed in (dilute) aqueous solutions of chloroform and of benzene.

The author believes that the swelling effect of aqueous solutions of organic substances is not so difficult to explain as has often been thought. It may be added that A. Frumkin (Moscow) has come at the same time as the author to an analogous explanation of these swelling effects.

It may be useful to remember that a large number of important technical processes, working with cellulose, starch or albuminoids are closely connected with the problem of the laws of swelling.

Considerations of space have made it necessary to omit consideration of these and also of other important facts about swelling. The reader may consult the second part of H. Freundlich's *Kapillarchemie* (latest edition) in order to find many particulars about them. In making a choice, the facts studied by the author himself were more fully discussed than certain other facts. By comparing H. Freundlich's review of the subject the reader will find it easy to correct the one-sidedness connected with the choice mentioned above.

For more explicit articles of the author on swelling, see Gesetze der Quellung, Koll. Beih., 9, 1, 1917; Quellung I. and II., Ergebn. d. exakt. Naturw. 3, 316, 1924, and 4, 154, 1925, Berlin, J. Springer; Das Problem der Quellung der Cellulose und ihrer Derivate Z. Cellulosechemie, 11, Heft 2, 1930; Micellartheorie und Quellung der Cellulose, in Kurt Hess, Chemie der Zellulose, Akad. Verlagsges, 1927, pp. 687-769.

#### GENERAL DISCUSSION.

**Dr. Speakman** (Leeds) said: The swelling which accompanies water adsorption by wool is mainly intermicellar in type. It has been shown that whereas the intermicellar spaces in the dry fibre will not admit molecules larger than n-propyl alcohol, the size of the spaces in the waterswollen fibre is as much as 41 Å.U. Nevertheless, intramicellar water adsorption does occur, as was deduced from the form of the curve expressing the change of rigidity of wool fibres with water adsorption. Rigidity falls in linear proportion to the amount of intermicellar water adsorbed (excluding gross pores), and the first 5 per cent. of water adsorbed by dry wool, which is without effect on rigidity, must therefore be intramicellar in type. Acids likewise penetrate the micelles, opening the cross-linkages between the peptide chains, which are thus freed from one another and separated to an extent varying inversely with the strength of the acid. Thus all three forms of swelling—intramicellar, intermicellar and permutoid—are to be found in the case of animal fibres such as wool.

Mr. G. F. Davidson (Manchester) said: Professor Katz mentioned the possibility that part of the decrease of the total volume of the system which takes place when a solid swells in a liquid might be due to the penetration of the liquid into fine pores in the solid. The difficulty is to define the volume of the solid, and I should like to point out a method of attack which has been used with cellulose and wood. Helium has a very small atom, so that pores which are inaccessible to helium are inaccessible to any swelling liquid, and this gas is not adsorbed at the ordinary temperature; hence specific volume measurements with helium as immersion medium may be regarded as giving the true specific volume. If the apparent specific volume in a swelling liquid is found to be lower than in helium, the contraction cannot be attributed to penetration of the liquid into pores. I have used this method for cotton cellulose 1 and found that whereas the specific volume was about 0.64 in helium, it was only 0.62 in water, giving an average apparent specific volume of 0.93 for the sorbed water at saturation. Stamm 2 has used the method for wood, and recently Filby and Maass 3 have employed it to measure the variation of the apparent specific volume of water sorbed on cellulose with the moisture content of the cellulose.

Dr. W. W. Barkas (Forest Products Research Laboratory) said: Professor Katz states that the volume contraction of the solid-liquid combination is due entirely to the contraction of the water—the specific volume of which, after sorption, being 0.7 to 0.6. Do not the experiments on which he bases his results measure only the specific volume of the aggregate and, if so, may not the measured change be due as much to compression of the solid as of the water? Volbehre, working on spruce flour, reaches similar experimental results but chooses to interpret them as a contraction of the wood, assuming the specific volume of the water to be unchanged. Is there any way of choosing between these two points of view?

Mr. Miles (Ardeer) said that the recognition by Professor Katz of a class of intramicellar swelling, in which the lattice expansion was continuous and did not proceed by sudden changes from one structure to another as in the "permutoid" class of phenomena, was significant of the increased flexibility of the ideas which were now thought to accord

<sup>&</sup>lt;sup>1</sup> Shirley Inst. Mem., **6**, 41, 1927; or J. Text. Inst., 18, T175, 1927.
<sup>2</sup> J. phys. Chem., **33**, 398, 1929.
<sup>3</sup> Can. Jour. Research, **7**, 162, 1932.

with the facts of swelling. The opinion had been held very generally that X-ray spots which seemed to show a continuous expansion of spacing were really due to the superposition, in varying ratios of intensity, of the spots of two definite compounds of the swelling substance and the liquid or of the swelling substance itself and one compound. The changes in the spacings of cellulose acetate in various organic

liquids had been explained in this way.

In most of the known instances of intramicellar swelling the X-ray diffractions are diffuse and it is difficult to exclude such an explanation on experimental grounds alone. Recent experiments, however, had provided an instance in which the diffractions were sharp enough for satisfactory measurements. The X-ray diagrams of trinitroramie immersed in dilute aqueous acetone showed a continuous contraction of the central distance of the intense inner equatorial spot, and this contraction was found to be different in 5, 7.5 and 10 per cent. acetone. Photometry of this spot in the range given did not reveal any change in the half-intensity width, so that the hypothesis of superimposed diffraction from two separate substances could not be applied. These measurements, as well as those of the separation-distance of the spots had been made in such a way as nearly to eliminate the effect of the scattered radiation—a precaution which is very necessary. Above 10 per cent. of acetone the expansion of the structure appears to continue, but there is an increasing degree of disorganisation due to lack of alignment of the micellar units until at about 70 per cent. of acetone the diagram of the definite structure compound which had been first obtained and so clearly reproduced by Trogus and Hess, was fully in evidence. The behaviour of nitrocellulose in acetone-water, therefore, affords an example of both the intramicellar and the permutoid varieties of swelling which have been distinguished by Professor Katz.

Professor H. Staudinger (Freiburg i. Br.) said: Up to the present swelling has mostly been investigated on systems which are very complicated in structure and, moreover, very sensitive, e.g., the proteins, the polysaccharides, and rubber. In order to obtain a more correct knowledge as to the relations between swelling properties and molecular structure, synthetic products of well-known structure ought first to be investigated. For instance in the case of the polystyrols the observation was made that hemi-colloidal polystyrols of a degree of polymerisation of 100 dissolve without swelling phenomena. The swelling phenomena increase with a rise in the degree of polymerisation, so that the polystyrols of highest molecular weight (degree of polymerisation of 1000-5000) dissolve only with very pronounced swelling. In the case of these products there has actually been proved to be a relation between the degree of polymerisation and the swelling properties. The same relations were then found for natural products. Hemi-colloidal degradation products of these materials, such as hemi-colloidal rubbers and celluloses, do not swell, in contrast with the corresponding eucolloidal products. Of course this refers to products which are capable of unlimited swelling. The swelling properties of such substances as are only capable of limited swelling are considerably more complicated, since in this case three-dimensional molecules exist.

**Dr. J. R. Katz,** in reply, said: In measuring the volume contraction of swelling the only thing we really measure is, of course, the diminution of the volume of the aggregate. It is a matter of theoretical speculation, whether we ought to ascribe this diminution chiefly to the change of the liquid or to the change of the solid. As the liquid is as a rule more

compressible than the micellae of the solid are, I think it probable that the volume contraction is, for the greater part, due to a change in the liquid. But, of course, the volume of the solid also will change.

In applying the van der Waals' theory of binary mixtures to the problem of swelling (see my paper) one does not make a distinction of this kind. One treats the micellae as large molecules and shows that then—as one molecule of the binary mixture is very much larger than the other molecule—the system must have certain properties, which are just the properties found in the experiments. One of them is the large volume contraction.

The methods described by Mr. Speakman, Dr. Sheppard, Dr. Davidson, and others, for measuring the spaces between the micellae in a swelling body present an important new line of research, attacking the problem of the volume contraction from an entirely new side. In discussing these results it may be necessary to distinguish the real swelling and the borderland between swelling and capillary imbibition (see paragraph one of my paper), possibly both present in the same solid. This makes it rather difficult to draw conclusions from them as to the nature of swelling. By studying at the same time the ultrafiltration through this swelling body we may be able to discuss this problem.

I agree with Professor Staudinger that synthetic polymerised substances may be very useful in studying swelling and its connection with high molecular weight. Unhappily most of these polymerised substances do not exhibit a sharp crystalline X-ray pattern, as do the natural substances. This is a serious drawback, as the change of the X-ray diagrams in swelling is one of the chief ways, probably at this moment the best we have, for penetrating into the intimate nature of swelling. But the synthetic polymerised bodies are sure to play in the future a much larger rôle in the problem of swelling than they have done hitherto.

#### THE SWELLING OF SILK.

By W. S. Denham and E. Dickinson.

(Received 9th September, 1932.)

This paper is concerned with experimental observations on the swelling of silk-fibroin in solutions of different hydrogen-ion concentrations, mostly salt (buffer) solutions in the  $p_{\rm H}$  range I-9, and in atmospheres of different relative humidities, as indicated by variations in the width or "diameter" of filaments of degummed mulberry silk. The observations in solutions of different hydrogen-ion concentrations give minimal values of the swelling in solutions of about the  $p_{\rm H}$  values I-4, 2-8, 3-8 and 4-7, which are or lie near to  $p_{\rm H}$  values that different observers have on other grounds assigned to be the isoelectric point of fibroin; those in atmospheres of different relative humidities show approximately the variation of the swelling with variations in the humidity. Similar observations on the much thicker fibres of silk gut that are prepared artificially from the silk-substance of the silkworm gave results in general agreement on the whole with those given by the filaments.

#### Material.

#### Filaments.

The filaments were separated from raw silk (Italian throughout, except for the use of Japanese in some of the humidity measurements) that had been degummed at 98° C. in two successive soap baths containing respectively I and  $\frac{1}{2}$  per cent. of soap, and then washed exhaustively in, successively, distilled water, faintly acidified water, faintly ammoniacal water, distilled water of  $p_{\rm H}$  about 5.

#### Ginat

The gut was drawn gut ("7x" diam., about 0.1 mm.) of the kind used for fishing tackle; portions were selected that a microscopical examination indicated to be most nearly of circular cross-section.

# Swelling in Solutions of Different Hydrogen-ion Concentrations. Filaments.

Silk filaments are highly irregular in thickness and in the contour of their cross-sections, and a large number of individual measurements is required to obtain a reproducible, representative value for the mean diameter of the filaments in a sample of silk; but the course of the variation in the filament-diameter with variations in the composition of the solution in which the silk is immersed can be followed with fewer individual measurements if under the same conditions they give consistently the same mean value. It was found that if, by means of the experimental arrangement described below, the diameter of each of 100 filaments is measured once at the same place, when the filaments are secured so that they cannot shift, the same mean value is obtained in repetitions of the series of measurements under the same conditions even although the conditions may have been changed and restored between the two series. 100 filaments were laid parallel to each other at intervals of about 0.2 mm. across a microscope slide to which they were fastened near its sides by means of a wax or a cellulose preparation; the filaments were kept moist during mounting. Two glass filaments of diameter about 0.01 mm. were then laid across the silk filaments parallel to the long side of the slide at a distance of about I mm. from each other and fastened to the slide at their ends in the same way. The width of a given silk filament was always measured at the same point between the glass filaments. The arrangement was completed by the addition of a cover glass the space between which and the slide was flooded by the solution. The measurements were made at a magnification of 500 diameters by means of a screw micrometer eyepiece.

Most of the measurements were made in buffer solutions and the differences in swelling in different solutions cannot therefore be ascribed solely to the differences in hydrogen-ion concentration as the solutions necessarily differ otherwise in their composition. It is likely, however, that the directions of the changes in the swelling due to the changes in the hydrogen-ion concentration are correctly indicated by these measurements in buffer solutions because they were the same when different buffers were used over the same  $p_{\rm H}$  range or when unbuffered solutions of acid or alkali were used. The buffer solutions were prepared as directed by Clark; <sup>1</sup> their hydrogen-ion concentrations were checked colorimetrically by means of indicators. The new solution was introduced

 $<sup>^{\</sup>rm 1}$  Determination of Hydrogen-ions, 2nd edition, 1922, pp. 99-117. The Williams & Wilkins Company, Baltimore.

at one side of the slide in a direction parallel to the silk filaments, the old solution being withdrawn at the other by means of filter paper. Two hours' contact between the filaments and the solution was sufficient for the attainment of equilibrium. After numerous changes of the solution the filaments might become recognisably disarranged and the observations were therefore continued with a new set of 100 filaments, a liaison between the two series of observations being effected by repeating on the new set the measurements made at the last one or two  $p_{\rm H}$  values on the old, for the mean diameter of the filaments in the two sets of 100 might be slightly different under similar conditions. These disarrangements occurred mainly at  $p_{\rm H}$  values greater than 7 when the wax was used as adhesive, owing to its disintegration; the cellulose preparation was a more satisfactory adhesive over the whole range of  $p_{\rm H}$  values. Overlapping determinations were likewise made when the buffer was changed otherwise than in the proportion of the constituents.

The mean diameters in scale divisions are given in Table I., of a set of 100 filaments over the  $p_{\rm H}$  range 4-2·2, in steps of 0·1 between 4 and 3·4, and in steps of 0·2 between 3·4 and 2·2. The mean diameters are given to three places of decimals of which at least two are significant. Citric acid-phosphate buffer.

$p_{\mathrm{H}}.$	Mean Diameter (Scale Divisions).			
4.0 3.9 3.8 3.7 3.6 3.5 3.4 3.2 2.8	4·958 4·929 4·914 4·945 4·965 4·995 5·014 5·011 4·979			
2.6	4.983			

5.001

5.017

TABLE I.

The curve, Fig. 1, summarises the results of numerous observations over the  $p_{\rm H}$  range of 1-9 involving six sets of filaments. Buffers: citrate-hydrochloric acid for  $p_{\rm H}$  1·0-2·4, phosphate-citric acid for  $p_{\rm H}$  2·2-7·0, borax-boric acid, sodium chloride  $p_{\rm H}$  7·0-9·0. The mean diameter for  $p_{\rm H}$  3·8 is taken as 100 and a connection between the different sets of filaments or between the different buffers is made by means of overlapping determinations.

2.4

#### Gut.

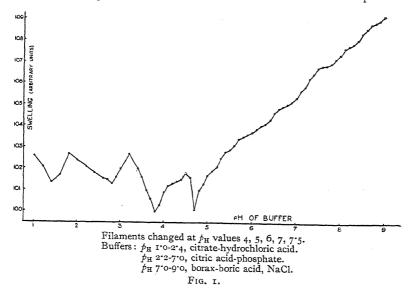
Similar but less regular results were obtained with silk gut in buffer solutions. It is considered likely meantime that improved methods may yield more regular results and eliminate some apparent differences in behaviour (which may, however, be real) between the filaments and the gut. Equilibrium between the gut and the solution takes longer to attain than between the filaments and the solution; for this reason short pieces of gut about 2 mm. long were used so as to have as large a surface as possible. Each of the four series of measurements in Table II.

	I.		II.		III.	IV·		
<i>p</i> <sub>H</sub> .	Mean Diameter.	<i>p</i> <sub>H</sub> .	Mean Diameter.	<i>₽</i> <sub>H</sub> .	Mean Diameter.	p <sub>H</sub> .	Mean Diameter.	
1.0 1.2 1.4 1.6	96·81 98·05 97·46 98·30	2·6 2·8 3·0 3·2	99·94 98·41 98·80 99·32	3·2 3·4 3·6 3·8 4·0	99.74 99.28 99.21 98.29 98.48	4·4 4·6 4·7 4·9	98·56 99·54 98·33 98·96	

TABLE II.—Gut in Hydrochloric Acid. Mean Diameters in Scale Divisions.

was made with 10 such pieces of gut, 10 measurements along each piece, or 100 measurements for each  $p_{\rm H}$  value. The pieces of gut were not stuck to the slide and may have moved during the measurements, which were made in solutions of hydrochloric acid the  $p_{\rm H}$  value of which was checked colorimetrically.

Further observations are in progress. The results of those already made indicate that minimal values of the swelling occur at the  $p_{\rm H}$  values 1·4 (approx.), 2·8 (approx.), 3·8 (where the swelling is least) and 4·7. Hawley Jr. and Johnson 2 on the basis of observations on the cataphoresis



and flocculation of suspension give the isoelectric range  $p_{\rm H}$  1·4-2·8. Nakajima ³ gives the optimum coagulation points at  $p_{\rm H}$  1·3 and 3·9 and regards the latter as being very near the isoelectric point; Shozo Bito ⁴ places the isoelectric point of tussah-fibroin in colloidal dispersion at  $p_{\rm H}$  2·85 from nephelometric observations; Denham and Brash ⁵ on chemical grounds give  $p_{\rm H}$  3·8 for the isoelectric point of fibroin; and Meunier and Ray ⁶ from observations on the swelling as determined by weighing gave  $p_{\rm H}$  4·2.

Ind. Eng. Chem., 22, 297, 1930.
 Bull. Seri. and Silk Ind. Japan, 4, No. 2, 2-3, 1931.
 J.T.I., 18 (Special Issue), T520, 1927.
 Chem. Abstr., 22, 2995, 1928.
 C.R., 184, 285, 1927.

Measurements of the length of silk filaments in different solutions have not yielded definite evidence of a variation in length associated with a variation in the hydrogen-ion concentration of the solution.

## Swelling in Atmospheres of Different Relative Humidities. Filaments.

The measurements of the lateral swelling of silk filaments in atmospheres of different relative humidities were made on filaments attached to a slip of glass which was secured to the glass roof of a cell, built on a microscope slide, in which the controlling liquid was contained in glass capsules. For a dry atmosphere phosphorus pentoxide was used. In the earlier series thirty measurements were made on each of three to six silk filaments, but in the later ones one measurement was made on each of 100 filaments as in the measurements of the swelling of silk in solutions. Shifting of the filaments is more frequent and causes more trouble in these measurements in air than in those in solutions, partly no doubt because, for observations on the humidity-swelling, they must be mounted when dry or air-dry and so become loose in wetter atmospheres whereas the filaments for observing the swelling in solutions are mounted moist. The shift is most frequent at the higher humidities especially at 100 per cent. relative humidity. The measurements here made at a mean temperature, uncontrolled, approximate 65° F.

In Table III. are given the results of three series of observations on filaments of Japanese silk that were brought by stages from a dry to a saturated atmosphere and then again by stages to a dry atmosphere. Instead of measuring the diameter in a saturated atmosphere it was necessary to flood the filaments with water as, otherwise, local condensations of moisture prevented accurate readings. The mean values are those for all the filaments (13) in the three series. Thirty measurements were made at intervals along the length of each filament.

TABLE III.—Mean Lateral Swelling of Filaments of Japanese Silk Per Cent. of Original Dry Diameter.

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Relative humidity, per cent. . . 30 60 90 100 90 60 30 0 Mean lateral swelling per cent. . . . 2·1 3·8 8·9 18·7 9·3 4·2 2·4 0·2
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These means of selected values for the Japanese silk are in good agreement with the means of 100 measurements, one on each of 100 filaments of Italian silk that are given in Table IV. The latter are thought to be the more exact. Nearly the same values are obtained when the mean diameters are calculated and then the mean lateral swelling, as when the ratios of the diameters of each filament at a given humidity to that of the dry filament are calculated and then the mean ratios; the latter are those given:—

TABLE IV.—Mean Lateral Swelling of Filaments of Italian Silk Per Cent. of Original Dry Diameter.

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Relative humidity, per cent. . . . 20 40 60 80 90 95 100 Mean lateral swelling per cent. . . . 1.6 2.4 3.5 6.1 8.4 11.1 16.3
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These mean values are probably fairly accurate for the particular filaments. It is calculated by Mr. E. A. Hutton of this laboratory that the probable error, if they are considered as representing the swelling of the sample of silk from which the filaments are taken, is 0.2 for the

swelling at 2.0 per cent. relative humidity and 0.7 for that at 100 per

The longitudinal swelling of silk filaments, dry to wet, is about 1.3 per cent.

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### THE TENSILE PROPERTIES OF SILK FILAMENTS.

By W. S. Denham and T. Lonsdale (British Silk Research Association).

(Received 7th September, 1932.)

The tensile properties of filaments of mulberry silk that are the subject of this paper were studied (I) by a recording extensometer. (2) by loading the filaments directly with weights, and (3) by stretching the filaments to a definite amount by a pull. The load-extension curves of short lengths of filament (about 5.5 cm.) broken individually in the extensometer were similar in form although they differed in their dimensions. From these curves average values per filament of the load and extension at the proportional limit and at break were obtained for various samples of silk as well as average values of derived quantities such as the tensile strength and Young's Modulus. The extensometer was also used to study the variation of the breaking load and extension of silk filaments with variations in the relative humidity or with the rate of the extension and for cyclic loading and unloading; but the persistence of residual effects after loading and unloading was more conveniently studied on longer filaments (40-50 cm.) by the methods of direct loading or stretching.

#### Material.

The continuous thread or "bave" from which the silkworm forms its cocoon is composite, consisting of two filaments or "brins" of fibroin cemented together by sericin or silk gum. When the gum is removed, as by treating the silk with a hot solution of soap, the component filaments can be separated; and as the bave has a length of from 1000 to 2000 metres, of which about one-half can usually be reeled, it is possible to obtain single filaments of almost any desired length. The ease with which very long filaments can be obtained facilitates the study of the influence of conditions on the tensile properties, because similar samples can more readily be prepared from a few long filaments than from more numerous shorter filaments taken indiscriminately. Against this advantage for experimental purposes possessed by silk stand the tenuity of the filament of mulberry silk (diameter 10-30  $\mu$ ), and the irregularity in the shape and size of its cross-section, qualities which demand delicate manipulation and the execution of a large number of individual measurements of any property in order to obtain a trustworthy mean value.

The filaments used in the work described in this paper were separated in the laboratory not directly from the cocoon but usually from the commercial product known as raw silk. Raw silk is prepared at the filatures by laying together without twist the baves from six or more cocoons; the thread of raw silk is thus composed of twelve or more filaments held together by the gum which had been temporarily softened by the hot water in which the cocoons were immersed during reeling.

The raw silk from which the long filaments were separated was degummed in the laboratory on a specially designed reel. This consists of three brass discs held together by a central axis, and by eight peripheral pins passing perpendicularly through the three discs. After winding the raw silk round the pins, two of the pins are withdrawn to allow for the contraction of the hank when wetted, and the reels are then immersed first in a I per cent. and then after rinsing in hot water in a  $\frac{1}{2}$  per cent. solution of soap in each bath for one hour at 98° C. After alternate treatments with faintly acidic and with faintly ammoniacal water, and finally with hot water, the silk is dried on the reels in air at the ordinary temperature. By manipulating a length of the degummed raw silk on a velvet-covered board, it is first separated into pairs of filaments (the original bave), and each pair of filaments is then separated into its components. Filaments up to 3 metres or more in length, thus separated, are cut into pieces of the required length.

#### Extensometer Measurements.

#### Extensometer.

The extensometer used was that designed by T. Lonsdale, in which tension on the filament under test produces torsion of a steel blade; the amount of this torsion is recorded by the consequent deflections in a vertical plane of a beam of light which falls on a photographic film. The elongation of the filament corresponding to the tension is proportional to the (corrected) horizontal movement of this film, which thus directly records the load extension diagram with rectangular co-ordinates. The vertical deflection of the spot of light on the film is about 0.5 cm. per gram of load on the filament; a horizontal movement of the film of 1 cm. corresponds to an elongation of the filament of 10 per cent. of its initial length of 5 cm. The average size of a load-extension diagram is about 2.5 cm. by 2.5 cm.

The film is held in a carriage which is normally moved horizontally by a plunger falling in a cylinder of oil; for cyclic loading and other experiments this arrangement is replaced by a lever mechanism by which the carriage may be moved in either horizontal direction. The carriage is attached by levers giving a 2:1 magnification to a clamp gripping a wire to which is secured the lower end of the filament. The upper end of the filament is attached by a wire and hook to the load-recording mechanism; the movement of this upper end of the filament being relatively very small, the elongation of the filament is governed almost entirely by the movement of the carriage, which, in turn, is controlled by the plunger. The plunger attains its final constant speed almost at once, so that except at the very beginning the filament is extended by moving the lower end with constant velocity, the upper end being almost stationary. After each filament breaks, the axis of zero load is recorded on the photographic film by making an additional traverse of the carriage.

The instrument is calibrated with respect to load by hanging weights on the hook attached to the load-recording mechanism, the corresponding vertical deflections of the spot of light furnishing the load scale. This calibration is statical, whereas the load-recording parts are in movement during the registration of a load-extension curve. There is thus the possibility of error caused by the inertia of these moving parts. The theory of this error for a somewhat different type of machine has been worked out by Shorter.2 He showed that the error is small if the natural time period of vibration of the recording system is small relative to the time taken in testing a specimen; and that it reveals itself in a somewhat wavy appearance given to the load extension diagram. Since some of the experiments to be described were concerned with breaking filaments as fast as the instrument would permit, it was thought well to find experimentally the actual magnitude of the error for this instrument, although it was suspected to be small owing to the high natural period of the recording system. To this end, a spiral spring wound from fine hard steel wire was mounted in the instrument and extended at the normal speed of working, and as slowly and as fast as the instrument would permit. The load-extension curves thus obtained were identical, and show that the inertia error is very small.

#### Mounting the Filament.

Before mounting a length of filament in the extensometer, a small piece of wire is attached to each end of it. The wire is warmed in the middle by means of a tiny gas flame, a blob of Faraday's wax is picked up by one end of it, and by means of tweezers the end of the filament is laid parallel to the wire to which it adheres when the just molten wax hardens. These operations can be executed without damaging the filament, but after each test the filament is examined, and the result for any filament that breaks at or near the wax is rejected.

#### Conditioning.

Each filament was conditioned, after mounting, for at least twentyfour hours in an atmosphere of the relative humidity at which the test was made. For relative humidities between 60 and 85 per cent. the filaments were conditioned and tested

in the atmosphere of the constant humidity chamber, duly adjusted to the required humidity; but for other humidities, below 60 or above 85 per cent. each filament was conditioned and tested in a separate closed tube which contained a controlling solution; the arrangement used is shown in section in Fig. 1. The filament (F) is mounted with a little slack between the copper wire (W), which is fixed in the cork, and the aluminium wire (A), which can slide through a narrow glass tube (T), also fixed in the cork. The tube contains some of the controlling liquid, such as a solution of sulphuric acid. Immediately before each test the tube is removed and mounted in the lower clamp and the aluminium wire in the upper clamp of the extensometer. The tubes containing filaments that were to be tested dry had a side tube below the cork through which, during the test, dry air issuing by the tube T could be passed to prevent the diffusion of atmospheric moisture into the test tube.

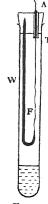


Fig. I.

<sup>&</sup>lt;sup>2</sup> J.T.I., T.501, 1923; see also Pierce, ibid., T.342, 1926.

#### Cross-Sectional Area of Filaments.

Cross-sections of filaments of mulberry silk are frequently of triangular outline, with the sides curved outwards; but they may be of other shapes, their contour may be re-entrant in places, and the filament is sometimes flat like a ribbon. By measuring the mean diameter and the mean area of numerous cross-sections from different parts of the sample of Italian silk used in most of the experiments, it was found that  $A = 0.84 \, \pi D^2/4$ , where A is the mean cross-sectional area and D the mean diameter. The same relation was found to hold in similar but less extensive series of measurements made on Japanese and Canton silks, and in fewer measurements (two series, each of 16) made on sections taken from different parts of a single long filament of the Italian silk. The diameter of each filament (length 5.5 cm.) was measured microscopically in two places immediately before mounting it on the extensometer, and the mean of all the diameters thus found in a series of tests was used to calculate from the above relation the mean cross-sectional area of the filaments used in the series. It might be suspected that the mean "diameter" of the filaments of a sample of silk, as determined by microscopical measurements of the filament viewed longitudinally, would be greater than the true mean diameter owing to a possible tendency of the filaments to lie on their broadest sides, but no appreciable error due to this cause was disclosed by a series of microscopical measurements made on filaments of the length used in the extensometer with the aid of a contrivance for rotating the filaments without torsion.

#### "Twin" Samples for the Study of the Effect of Conditions.

To study the comparative behaviour of the filaments under different conditions, for example under different relative humidities, a long filament is cut into a number of short lengths which are numbered according to their original position in the undivided long filament. The odd numbers are placed in one of two groups, and the even numbers in the other, and the filaments in the one group are broken singly at the one relative humidity, and those in the other group at the other relative humidity. The average values of the property in question derived from each set of curves are then compared. It is found that this procedure to some extent overcomes the difficulties caused by the irregularities of the filaments and that the results thus obtained are more definitely significant than when the two groups of short lengths of filament broken under different conditions are taken indiscriminately from different filaments of silk.

#### Load-Extension Curves.

Some typical load-extension curves for silk filaments as recorded by the extensometer are shown in Fig. 2. Two portions can be distinguished in the curves for filaments tested in atmospheres of a relative humidity less that 85 per cent., namely an initial straight line portion representing proportionality within the accuracy of the record between the load and the extension, and beyond this a curve approximately parabolic in shape which bends over towards the extension-axis. The limit of proportionality is usually sharply defined for filaments tested dry, and it is still fairly well defined, but at a much less load, at 85 per cent. relative humidity; but in the curves for filaments tested over water (100 per cent. relative humidity) or in water the straight-line portion has practically disappeared and the curve is nearly parabolic throughout.

## Mean Load per Filament and per Sq. Cm., and Extension, at Break, and at Limit of Proportionality: Young's Modulus.

By means of a suitable graticule the load and extension at break and at the limit of proportionality were read off from the curves for a sample of Italian silk (485 curves), another sample of Italian silk (52 curves), and a sample of Canton silk (80 curves), and the mean values of each quantity were calculated for each sample. From these mean values and the mean cross-sectional areas computed from the mean diameters, mean

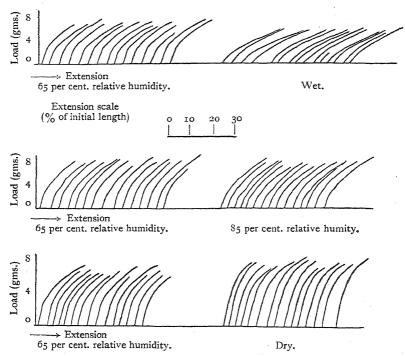


Fig. 2.—Load-extension curves of silk filaments obtained with extensometer selection from records given by "twin" samples broken at different humidities.

values were calculated for the load per square centimetre at break (tensile strength) and at the proportional limit. From this (mean) load per square centimetre at the proportional limit and the corresponding mean extension a value was derived for Young's Modulus. These "mean" values for the tensile strength, load per sq. cm. at the proportional limit and Young's Modulus, given in Table I, are not strictly to be so described, as they were obtained as indicated, and not by calculating the value for each individual filament and then taking means.

The mean values in Table I are not necessarily representative for the different varieties of silk within each of which filaments of widely different diameters and breaking loads may occur, whilst a complete identity of treatment of different samples, for example during degumming, cannot

TABLE I.—Mean Diameter, Breaking Load, Extension at Break, Load at Proportional Limit, Load per Sq. Cm. at Break (tensile strength), Load per Sq. Cm. at Proportional Limit and Young's Modulus of Mulberry Silk Filaments.

Relative Humidity,	65	Per	Cent.
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Material	Ital		
Material.	Sample 1.	Sample 2.	Canton.
No. of filaments tested	485 0.00130 6.8 25.6 2.17	52 0·00128 6·7 24·7 2·35 3·1 6·1	80 0.00078(4) 2.6 18.4 0.92 2.1 6.4
Load at proportional limit (dynes per sq. cm. × 10°) Young's Modulus (dynes per sq. cm. × 10¹0.)	1·91 7·22	2·13 6·79	2.23

be ensured; the extreme values for the 485 filaments of sample I of the Italian silk were: breaking load I·8 and IO·0 grams, extension at break 2·3 and 43·7 per cent., diameter 0·0007 and 0·0023 cm. Thus the good agreement between the mean breaking loads of the two samples of Italian silk may be accidental. Between different silks there is a much closer approximation of the loads at break and at the proportional limit when expressed per unit area than when expressed per filament; this levelling effect of introducing the diameter into the calculations is very noticeable in Table I, where the Canton silk, which has a small filament-diameter, is compared with the Italian.

# Effect of Humidity on Load and Extension at Break, and on Load at Proportional Limit.

In general, the breaking load and extension at break of a textile fibre depends upon the humidity. Thus the breaking load of single cotton hairs increases with increasing humidity, the rate of increase becoming probably negligibly small at relative humidities above 66 per cent.; the extension at break of cotton hairs likewise increases with increasing relative humidity.<sup>3</sup> The breaking load of wool fibres decreases and the extension at break increases with increase in the relative humidity,<sup>4</sup> and in this respect silk resembles wool; but the load-extension curves for the two fibres, wool and silk, are different in their general shape, those of silk resembling the curves for cotton hairs.

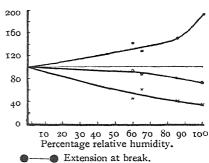
Typical load-extension curves for silk filaments are given in Fig. 2, those on the left-hand side obtained at 65 per cent. relative humidity for alternate short lengths cut from a long filament and those on the right the corresponding curves obtained at a different humidity for the other series of alternate lengths cut from the same filament according to the method already described for the preparation of comparative samples. The mean breaking loads at the same humidity of two groups,

 $<sup>^3</sup>$  Mann, J.T.I., T.253, 1927; Brown, Mann & Piercei ,bid., T.186, 1930.  $^4$  Speakman, J.T.I., T.472, 1926.

each consisting of twenty alternate lengths cut from a single filament about 3 metres long, do not usually differ by more than I to 2 per cent.; if the two groups are similarly formed from three filaments, each I metre long, the agreement is not so good, but it is much closer than that between groups of filaments taken at random. Differences greater than 3 or 4 per cent. between the breaking loads or other quantities of two groups formed from a 3-metre filament that are tested at different humidities, are probably significant of real differences due to the difference of the humidities.

The comparisons made by this method showed that the breaking

load of silk filaments is less and the extension at break greater at the higher than at the lower relative humidity, and that the load at the proportional limit decreases steadily from dryness The errors of wetness. measurement of the small extension at the proportional limit are too large to allow the instrument to give a certain indication of any change in this quantity with the humidity. These comparisons are summarised in the curves of Fig. 3 in which the various quantities at any humidity are expressed relatively to the corresponding quantities for the dry filaments taken as The curves show the fall



O Breaking load. × — × Load at proportional limit.

Fig. 3.—Breaking load, extension at break, load at proportional limit of silk filaments at various humidities. (Each quantity arbitrarily taken as 100 at

o per cent. relative humidity.)

of the breaking load, the sharper fall of the load at the proportional limit, and the increase of the extension at break with increasing humidity; and that the straight line portion is a smaller proportion of the total curve for successively higher values of the relative humidity.

#### Effect of Humidity on Tensile Strength and on Load per Sq. Cm. at Proportional Limit.

By taking account of the change in diameter (swelling) of silk fila-

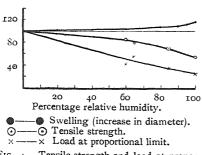


Fig. 4.—Tensile strength and load at proportional limit of silk filaments at various humidities-results corrected for swelling.

ments with humidity, measurements on which are recorded elsewhere,5 the effects of humidity on the tensile strength and on the load per sq. cm. at the proportional limit of silk filaments were derived from the values of the load at break and at the proportional limit. These effects are represented by the curves of Fig. 4, in which as before the loads per sq. cm. are taken as 100 for the dry filaments. With increasing humidity the loads per sq. cm. fall

<sup>&</sup>lt;sup>5</sup> Denham and Dickinson (Trans. Faraday Soc., 29, 1933).

more rapidly than the corresponding loads per filament, owing to the swelling of the filaments with increasing relative humidity.

#### Effect of Rate of Extension on Load and Extension at Break.

The values of the breaking load, and the extension at break, of a textile fibre depend upon the rate at which the fibre is extended. Thus, Mann and Pierce <sup>6</sup> found that at 66 per cent. relative humidity the mean breaking load of a sample of cotton hairs increased from 4·1 to 5·5 gm. as the rate of loading was increased from 0·003 gm. to 1 gm. per second, but was sensibly constant at higher rates of loading. For Cotswold wool fibres in water, Speakman <sup>7</sup> found that the breaking load and the extension at break increased with the rate of loading; his observations were made at rates below 0·25 gm. per second.

Silk behaves similarly. In the extensometer as ordinarily used the lower clamp moves at the rate of 0.094 cm. per second, but the rate can be varied. "Twin" samples of filaments were prepared, and the lower clamp was moved as fast as the instrument would permit in breaking the filaments of the one group (0.24 cm. per second; 5 per cent. extension per second), but as slowly as possible in breaking the filaments of the other group (0.009 cm. per second; 0.2 per cent. extension per second). Comparisons made in this way in a dry atmosphere, in one of 65 per cent. relative humidity, and in a wet atmosphere gave higher values for the "fast" measurements at each humidity, as shown in Table II.

TABLE II.—Effect of Rate of Extension on Breaking Load and Extension at Break of Silk Filaments.

Relative Humidity.	"Fast" Values as a Percentage of "Slow" Values.				
Per Cent.	Breaking Load.	Extension at Break.			
o (dry)	115	124			
65	(i) 116 (ii) 117	(i) 110 (ii) 115			
Ioo (wet)	113	104			

"Fast" 5 per cent. extension per second. "Slow" o'2 per cent. extension per second.

In so far as these results for two rates of loading indicate, the increase in breaking load at the higher rate of loading is independent of the humidity, whereas the corresponding increase in the extension at break is less at the higher humidity.

#### Cyclic Loading.

In some cyclic experiments made with the extensometer, a traverse of the carriage was made sufficient to extend the filament by 2 per cent., and the carriage was then returned immediately to its initial position, the whole cycle taking not more than 3 to 4 seconds; a 2 per cent. exten-

<sup>&</sup>lt;sup>6</sup> J.T.I., T.82, 1926.

sion is somewhat less than the mean extension at the proportional limit but may exceed this limit for an individual filament owing to the differences that exist between different filaments in this as in other respects. It was found nearly always with filaments tested wet or dry that the record of the contraction coincided exactly with that of the extension, even after several cycles had been made with the same filament.

#### Composite Nature of Strain Produced by Loading.

Following Pierce, it is convenient to distinguish three types of strain produced in a textile material by any stress, namely, an elastic strain which disappears instantaneously after removal of the stress, an epibolic strain which disappears after a finite time, and a plastic strain which is permanent. In the cyclic experiments in the extensometer described above, neither epibolic nor plastic strains show themselves in silk filaments when the strain is rapidly applied and removed; but direct loading experiments showed that the strains produced in silk filaments, even by very small stresses, are composite; for small stresses they are almost entirely elastic and epibolic, but as the stresses become larger the irre versible plastic component becomes increasingly important.

#### Direct Loading.

#### Apparatus.

Long filaments separated as already described were cut into lengths of 40 to 50 cm., which were hung in a box fitted with windows. To a wire hook attached to the lower end of each filament weights were hooked on or off without shock by means of a platform which could be raised or lowered by means of a screw. The total length of the filament was measured with a cathetometer and changes in its length due to loading or unloading were measured for greater accuracy by means of a travelling microscope with which the movements of the lower end were observed, precautions being taken to ensure that the movement observed was due solely to a change in length of the filament. The observations were made in a constant humidity chamber.

#### Single Load.

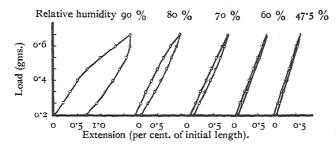
A noticeable lengthening of the filament occurred after cycles of loading and unloading, each complete cycle occupying 4 minutes, at 75 per cent. relative humidity. In an experiment in which the filament was loaded with 0.75 gm. in one stage, and unloaded, the elongation immediately after finally removing the load after thirteen cycles was 0.53 per cent.; after one hour the elongation was 0.35 per cent.; and after 120 hours the filament had returned exactly to its original length. In other experiments filaments from the same sample of silk did not return exactly to their original lengths, after numerous cycles under 0.75 gm.

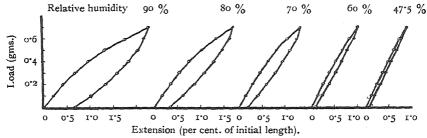
#### Loading by Increments.

In other cyclic experiments a total load of 0.7 gm. was imposed in increments of 0.1 gm. added after successive intervals of exactly one minute, and then removed similarly in stages, the complete cycle taking

fourteen minutes. Cycles of this kind were made with each of a number of filaments at the relative humidities 90, 80, 70, 60 and 47.5 per cent. successively, the filaments being duly conditioned after each change of the humidity before making the cycle. At each humidity after the cycle of maximum load 0.7 gm. was completed two further similar cycles of maximum load 0.5 gm. were made; these gave results very similar to those of the 0.7 gm.-cycle, but they are not now discussed.

similar to those of the 0.7 gm.-cycle, but they are not now discussed. The curves shown in Fig. 5 are typical of the results obtained. The width of the cycle is an indication of the amount of epibolic strain; it is seen that this strain is small at low humidities, but is larger the higher the humidity. This increase is relatively large above 80 per cent. relative humidity, and it is interesting to note that the increase in swelling above 80 per cent. is also relatively large (Fig. 3). It will be seen also that for the successively higher humidities these curves are the more





Upper curves, filament No. 1. Lower curves, filament No. 2. Fig. 5.—Cyclic loading curves for silk filaments at various humidities.

inclined to the extension axis owing to the fall in the value of Young's Modulus with increasing humidity.

Values of Young's Modulus were calculated from the results obtained in these slow loading experiments for five long filaments, from measurements on the slope at the origin of the initial portion of the cyclic curves. Here, presumably, the influence of the epibolic strain is small. The diameter of each filament was measured in numerous places at about 65 per cent. relative humidity, and the diameter at the various humidities calculated from this mean diameter and the swelling figures. Young's Modulus at each humidity is thus referred to the diameter at that humidity. The filaments used were taken from Japan filature. Table III gives the results obtained.

The results are in good agreement with those obtained for Italian silk at 65 per cent. relative humidity from the extensometer measurements (Table I).

TABLE III.—Young's Modulus of Silk Filaments (Japanese) at various Relative Humidities.

Relative Humidity.	Young's Modulus
Per Cent.	dynes/sq. cm.
47°5	10·0 × 10 <sup>10</sup>
60	8·9 ,,
70	7·1 ,,
80	6·3 ,,
90	5·1 ,,

#### Stretching.

The recovery of silk filaments after extension beyond the proportional limit has been studied in various series of observations, from among which the following are described.

#### Apparatus and Method.

The filament, provided with wire hooks at each end, was suspended in water under the tension of the lower hook (0.05 gm.) to remove kinks, and then transferred to a tube containing sulphuric acid, or a mixture of sulphuric acid and water, afterwards closed, in which it hung freely. The length of the filament was measured after twenty-four hours, and it was then stretched about 5 per cent. of this length by means of a wire inserted through a tube of narrow bore (afterwards closed) which passed through the liquid at the bottom of the wider tube, and the length of the filament was measured after successive intervals of time. The results are summarised in Table IV.

TABLE IV.—RECOVERY OF DRY FILAMENTS OF ITALIAN SILK ABOUT 50 CM.

LONG AFTER STRETCHING (OVER CONCENTRATED SULPHURIC ACID).

	Filamen	t No.			ı.	2.	3.	4.
	per cent. tion per ce	nt.:	•		5.04	5.03	5.11	5.15
	r instant re		у.	.	1.51	1.61	3.58	1.86
,,	15 second	s.	٠.	.	1.11	1.31	1.12	1.55
,,	r minute	e .			1.01	1.21	1.02	1.44
,,	5 minute	es.		.	0.01	1.11	1.02	1.24
,,	1 hour			.	o.81	1.00	0.83	1.13
,,	1 day	-			0.71	0.80	0.71	1.03
,,	2 days			.	0.71	0.70		0.93
,,	3 ,,	-	•	-	o·6o	0.60		_

Similar measurements were made at 65 per cent. relative humidity and in water. Some of the results obtained are given in Table V.

Taking the results in Tables IV and V together, it will be seen that the results for different filaments under the same conditions differ somewhat in magnitude.

TABLE V.—RECOVERY OF FILAMENTS OF ITALIAN SILK ABOUT 50 CM. LONG AFTER STRETCHING AT 65 PER CENT. RELATIVE HUMIDITY AND IN WATER.

		65 Per C	ent. R.H.	In Water.	
Filament No.		ī.	2.	ī.	2.
Stretch per cent Elongation per cent. :	•	5.00	5.00	4.76	4.97
After instant recove	erv .	1.8	2.0	1.05	1.39
" 15 seconds .	٠.	1.4	1.6	0.95	1.00
" I minute .		1.3	1.2	0.86	0.99
" 5 minutes.		1.3	1.3	0.86	0.89
" I hour .		1.0	1.3	0.76	0.79
,, rday .		0.9	I-I	0.57	0.79
,, 2 days .		0.9	I.I	0.48	
" 3 "· ·	•	0.0	I.I.		0.79
				1	1

The rate of recovery decreases rapidly, and the residual elongation is still considerable after several days.

The authors are indebted to Mr. Frank H. Wilkinson for making many of the observations referred to in this paper, and to Dr. A. L. Allen for many of the direct loading results which have been selected from his extensive experimental data.

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# NOTE ON THE "REGAIN" OF SILK OF DIFFERENT ORIGINS.

By WILLIAM S. DENHAM AND A. L. ALLEN.

Received 9th September, 1932.

A comparison of samples of degummed Mulberry silk (silk-fibroin) of different origins (Italian, Japanese, Chinese), has revealed no significant differences between their contents of hygroscopic moisture ("regains") under given conditions; the regain of mulberry silk was always less than that of tussah, which was included in the comparison. Several series of observations were made with approximately the same weight of each kind of silk in any one series; in the different series the weight used of each kind of silk varied from 0·3 to 2 grams. In each series the various samples were exposed simultaneously at 25° C. in the same desiccator, the relative humidity of the atmosphere in which was controlled by means of a mixture of sulphuric acid and water, until their weights were constant; each sample was contained in a separate weighing bottle, which was closed before the bottle was removed from the desiccator for weighing; the bottles were weighed at the laboratory temperature (18° to 20° C.). The originally moist samples were weighed after they had attained

hygroscopic equilibrium with atmospheres of successively lower relative humidities (desorption) and again, after drying, when they had attained equilibrium with atmospheres of successively higher relative humidities (absorption).

The regain was always greater during desorption than during absorption, at the same relative humidity, and the general form of the regain-

humidity relation is similar to that for other textile fibres.

The following figures for desorption regains refer to raw silk that had been degummed at 98° C. in two successive soap baths containing respectively I and  $\frac{1}{2}$  per cent. of soap, and then washed exhaustively in, successively, distilled water, slightly acid water, slightly ammoniacal water, distilled water ( $p_{\rm H}$  about 5); ash of the silk about 0.03 per cent. The samples of about 0.1 g. of silk were weighed on the microbalance. The regains are referred meantime to the constant weights obtained by drying the samples over concentrated sulphuric acid.

#### DESORPTION REGAINS.

Relative hu	ımidit	y, per	cent.		92.8	79.7	53.7	40	21.5
Italian . Chinese Japanese Tussah .			•	•	16·9 16·9 17·0	12·2 12·2 12·3 12·8	9·3 9·3 9·3	7.5 7.6 8.0	5*4 5*3 5*3 5*9

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#### SOME OBSERVATIONS ON THE CHEMICAL DE-GRADATION OF LINEN CELLULOSE.

By C. R. Nodder.

Linen Industry Research Association.

The three most important chemical or physico-chemical methods which have been in use for estimating the degree to which linen cellulose has been degraded by chemical attack are the determination of (a) viscosity in cuprammonium solution, <sup>1, 2</sup> (b) solubility number, <sup>3</sup> and (c) copper number. <sup>1</sup> A considerable mass of data bearing on the interrelationship of these properties has been accumulated and, although much remains to be done, it may not be premature to attempt the formulation of a working hypothesis directed towards the explanation of the observed relationships. Such a hypothesis will have value if it suggests promising lines of further investigation.

Oxidative attack and attack by acids may take numerous forms and it appears desirable in the first place to restrict attention mainly to a

<sup>&</sup>lt;sup>1</sup> Butterworth and Elkin, L.I.R.A. Memoir, No. 63, 1929.

<sup>&</sup>lt;sup>2</sup> Kinkead, J. Text. Inst., 22, T411, 1931. <sup>3</sup> Nodder, J. Text. Inst., 22, T416, 1931.

comparison of two of these, rather than to attempt the somewhat bewildering task of finding a hypothesis which will cover all known forms of attack. This is all the more desirable if attention is confined to linen cellulose, as information relating to some forms of attack is as yet meagre, or lacking.

The two important forms of attack which will be mainly considered are (a) that produced by approximately neutral hypochlorite solutions,

and (b) that produced by steeping or boiling in dilute acids.

It is desirable at this point to consider briefly the properties of typical "grey" linen materials, that is, materials which have undergone no chemical treatment. Here any degradation of the cellulose which has occurred has, generally speaking, taken place either while it was still in the plant or during the processes of retting and drying. The solubility number of such materials is normally about 2.0 and it appears that this value is made up, perhaps to an approximately equal extent, of two parts, one representing a slight degradation of the cellulose and one representing reducing non-cellulosic impurities not removed by the preliminary boil in dilute caustic soda. For a high quality Courtrai line a solubility number as low as 1.7 has been observed, while for low quality dew-retted flaxes a solubility number as high as 4.0 is not uncommon. Such observations suggest that a completely undegraded pure linen cellulose would have a solubility number of practically zero.

The log. viscosity of cuprammonium solutions, containing 2 per cent. of cellulose, is typically about 3.0 for grey linen but may exceed 4.0.

The copper number of grey linen is normally about 2.0. The reducing substances present are almost entirely non-cellulosic impurities, and after thorough scouring with caustic soda a copper number of 0.2 or less may be obtained. The materials which yielded the data \* considered in this paper were thoroughly scoured, and had a copper number of this order, before they were subjected to the oxidising or acid treatments referred to.

Very numerous determinations on materials oxidised with hypochlorite solutions have shown that the points obtained by plotting solubility number against viscosity † lie fairly closely about a curve which is represented by the equation

$$\frac{6}{\sqrt{S-1}} = \log \eta_2 + 1.85 \qquad . \qquad . \qquad . \qquad (1)$$

where S = solubility number and  $\eta_2 =$  viscosity of a 2 per cent. solution in cuprammonium. The viscosity,  $\eta_0$ , of the cuprammonium itself has log.  $\overline{2}$ ·15. Consequently

log. 
$$\eta_2 + 1.85 = \log_{10} \left( \frac{\eta_2}{\eta_0} \right)$$
.

The points plotted refer to materials from various sources treated with chemics of acid, neutral and alkaline reaction and cover solubility numbers varying from 2.0 to 50.0.

If a solubility number of 1.0 may be regarded as arising from reducing non-cellulosic impurities, and perhaps also to slight oxidation of the

\* These data have been, or will be, set forth in publications of the Linen Industry Research Association.

† It is sometimes convenient, for the sake of brevity, to use the term "viscosity" to mean the log. viscosity of a 2 per cent. solution of the cellulose in cuprammonium.

cellulose during the solubility number determination, it would follow that the equation  $\frac{6}{\sqrt{S}} = \log \left(\frac{\eta_2}{\eta_0}\right)$  closely represents the relation between

the solubility number of a pure, hypochlorite oxycellulose and its vis-

cosity in cuprammonium.

Data so far available for linen cellulose degraded by acids are less extensive than those for oxidised cellulose, but for three different scoured yarns, steeped in hydrochloric or sulphuric acid up to 10 N strength at room temperature, or at temperatures up to the boiling point for acids up to N strength, the points obtained by plotting solubility number against viscosity lie fairly closely about the curve represented by the equation

$$\frac{4\cdot 4}{\sqrt{S-1}} = \log \eta_2 + 1\cdot 85 \qquad . \qquad . \qquad (2)$$

The points plotted totalled over fifty and cover solubility numbers

ranging from about 2.0 to over 50.0.

Where the solubility number,  $S_1$ , of the original scoured yarn exceeds 2.0 owing, presumably, to oxidative attack during fibre extraction or scouring, better agreement between observed values and values calculated from the equation is obtained, as might be expected, if  $\sqrt{S-(S_1-1)}$  is written in place of  $\sqrt{S-1}$ .

It appears, therefore, that the equation  $\frac{4\cdot 4}{\sqrt{S}} = \log_{10} \left(\frac{\eta_{2}}{\eta_{0}}\right)$  represents

fairly closely the relation between the solubility number and viscosity of a pure hydrocellulose, prepared as indicated, a solubility number of I.o again being assumed to arise from reducing non-cellulosic impurities and slight oxidative attack during the actual determination.

For hydrocelluloses prepared by baking linen cellulose impregnated with dilute acids the equation given above appears not to represent satisfactorily the relation between solubility number and viscosity, the points so far obtained tending to be nearer the curve obtained with

oxycelluloses.

The relation between solubility number and viscosity enables, in many cases, a conclusion to be drawn as to whether degradation in a particular case was caused by hypochlorite or by acid attack. If the point lies above, or close to, the curve corresponding with equation (I) the former is indicated; if it lies below, or close to, the curve corresponding with equation (2) acid attack is indicated. Uncertainty arises when the point lies more or less mid-way between the two curves, and where degradation by acid baked into the material or by very strong sulphuric acid cannot be ruled out, and also, of course, where degradation may have been caused by agents other than those now under consideration.

We may now refer briefly to some further relationships between the

properties under consideration:-

(1) For solubility numbers greater than about 10.0 a given copper number corresponds with greater degradation, as indicated by viscosity or solubility number, in the case of materials boiled or steeped in dilute acids than in the case of materials attacked by approximately neutral hypochlorite solutions. Thus a copper number of 2.5 corresponds with a solubility number of about 25.0 for the former and about 17.0 for the latter.

- (2) For a given viscosity a material degraded by dilute acid has a considerably lower copper number than a material degraded by neutral chemic.
- (3) A material degraded by dilute acids loses very little more in strength when boiled with dilute caustic soda, whereas a material degraded by hypochlorite attack shows a very considerable further loss in strength when so boiled. Viscosity gives, in general, a good indication of the total loss in strength which may be expected when a linen yarn is degraded by dilute acid or by hypochlorite and subsequently boiled in dilute caustic soda.

Having indicated the foregoing observed relationships, we may consider briefly some further aspects of the properties with which we are concerned.

#### (1) Fibre Structure, 4, 5, 6.

The wall of a flax fibre is composed of numerous cellulosic layers, arranged concentrically about the fibre axis. Each layer has a fibrillar structure, the fibrils (which are visible under the microscope after suitable treatment) being arranged in left-handed spirals. The fibrils are regarded as composed of bundles of chains of cellulose micelles, the longest dimension of the micelles being parallel to the long axis of the

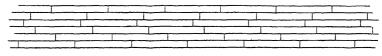


FIG. 1.

fibrils. In accordance with recent views, the structure of a fibril might be represented as in Fig. 1.7

Each unit in this diagram represents a micelle, or group of chains of glucose units, perhaps some two hundred glucose units in length. The transverse divisions represent, of course, the ends of these micelles.

#### (2) Viscosity.

The high viscosity of solutions of undegraded cellulose is presumably due to the great length of the micelles which form the disperse phase. The lowering of viscosity caused by chemical degradation appears to be satisfactorily explained as due to the shortening of the micelles.

## (3) Solubility Number.

The material dissolved out by the cold caustic soda solutions employed in the solubility number method must be regarded as degraded The cellulose remaining behind is undegraded cellulose, that is, it is essentially what is usually known as a-cellulose. Microscopic examination of fibres remaining after the caustic soda treatments

<sup>&</sup>lt;sup>4</sup> Reimers, Mitt. Deut. Forschung. Institute f. Textilstoffe in Karlsruhe, pp. 109-282, 1920-21.

<sup>&</sup>lt;sup>5</sup> Nodder, (a) J. Text. Inst., 13, 161-71; 213-19, 1922. (b) Trans. Faraday Soc.,

 <sup>20, 251, 1924.</sup> Searle, J. Text. Inst., 15, T371, 1924; el Kelaney and Searle, Proc. Roy. Soc., 106B, 358, 1930.
7 Cf. for example, Fig. 42, p. 62, in Mark's Physik u. Chemie der Cellulose,

Berlin, 1932.

shows that the characteristic fibre-structure still persists, the concentric layers and fibrils in the wall being still visible. It appears that the cellulose which goes into the solution comes from all the layers of the cell wall and does not consist, for example, of more highly degraded material from the outer layers. The removal of the degraded cellulose may be regarded as a desorption action, the particles of cellulose which are removed being small enough to pass out through the fibre walls. The process may be compared to the partial removal of a direct dye from a fibre by immersion in water. It appears reasonable to assume, therefore, that the solubility number is determined by the quantity of cellulose particles which are small enough to pass out of the fibre under the conditions of the determination. It must be remembered that the solubility number method involves a preliminary boil in a dilute caustic soda solution. This treatment removes the degraded cellulose which causes the reduction of copper in copper number determinations, but does not remove the degraded cellulose removable by the cold, strong caustic soda (10N - 2N). The swelling of the fibre in the cold, strong caustic soda, involving the lateral separation of the micelles, must be regarded as the essential condition which allows this latter form of degraded cellulose to be removed. A highly degraded material may lose 20 per cent. to 30 per cent. in weight when boiled with dilute alkali and still lose a further 50 per cent. in weight in the solubility number determinations.

#### (4) Copper Number.

An increase in the copper number of a cellulosic material by chemical attack may be regarded as due to the production of groups of an aldehydic nature by hydrolysis or oxidation of the cellulose. In the case of oxidative attack the possible production of acid as well as aldehydic groups must be considered. While the presence of aldehydic groups may be regarded as responsible for the reduction of the copper, the loss in weight of the material when heated with dilute alkalies must be due to the removal of cellulose which is sufficiently degraded as to be soluble under these conditions.

An attempt to formulate a hypothesis to account for the relationships which have been observed may be made as follows. This involves a few simple assumptions which, while not at present supported by any direct experimental evidence, are capable, at least in some cases, of being checked by experiment. Only the cases of attack by approximately neutral hypochlorite solutions or by dilute hydrochloric or sulphuric acid are considered, but similar reasoning should be applicable to other forms of chemical degradation if the assumptions are correct.

In the first place it appears that all the phenomena of chemical degradation are consistent with the view that the attack is localised at certain positions along the chains of cellulose molecules.\* In order to account for the residual strength of degraded fibres which have been boiled in dilute alkali it also seems necessary to assume that the points of attack are not, in general, arranged in planes at right angles to the fibrils, but are either distributed more or less at random or lie in planes

<sup>\*</sup> In this connection the possibility must be considered of a connection between the distribution of the points of attack and the "planes of segmentation" observable in tendered fibres after swelling with caustic soda, 50, 6.

which run obliquely to the fibrils. On these assumptions a partly degraded fibril might be represented as in Fig. 2 in which the shaded portions represent regions of modification.\* The presence of these modified regions causes a certain amount of weakening, but, as they still form parts of the chains, they may contribute towards the mechanical strength of the structure. The further loss in strength caused by boiling in dilute alkali may be regarded as due to the removal of the modified regions. The residual strength will depend largely on the lateral union of the micelles (by residual affinity). The fragments of micelles, presumably below a certain limiting size, such as those indicated by crosses in Fig. 2, may be regarded as those which pass out of the fibre in solubility number determinations, the strong, cold caustic soda having loosened the lateral union of the micelles.

The following assumptions are now made:-

- (a) Each region of modification contributes much less (say, about half) towards the copper number in the case of acid attack than in the case of oxidative attack.
- (b) In the case of acid attack the regions in which modification may occur are limited. We shall assume that such regions are limited to positions at the middle of each micelle or at a quarter of a micelle length from either end. It is also assumed that quarter micelle fragments



Fig. 2.

(or any smaller fragments) can pass out of the fibre in the solubility number determination. Other fractions might be chosen provided they were suitably related to the fractions considered under (c), below.

(c) In the case of oxidative attack, also, it is assumed that the attack is limited, but in this case to regions near the ends of the micelles, so that micelle fragments much smaller than a quarter are separated off, let us say one-sixteenth.

(d) It is assumed that in cuprammonium solution the micelles break at the regions of modification.†

Fig. 3 is intended to represent part of a chain of micelles composing a fibril such as is illustrated in Fig. 1. Six micelles are represented.

Fig. 4 is to represent two chains of micelles from two celluloses of the same copper number, the one (A) having been degraded by dilute acid and the other (B) by neutral hypochlorite. The shaded portions represent regions which have been modified. It will be obvious that (A) will represent a cellulose having a lower viscosity and a higher solubility number than that represented by (B). For, firstly, the average length of the micelles is much greater in (B) than in (A) and, secondly, the solubility number, by our assumptions, may be taken as represented by the portions indicated with crosses, these being small enough to pass

\* If the regions of modification lie in, or approximately in, "planes of segmentation" (i.e., at right angles to the fibre axis), they will lie in, or nearly in, planes oblique to the axes of the fibrils.

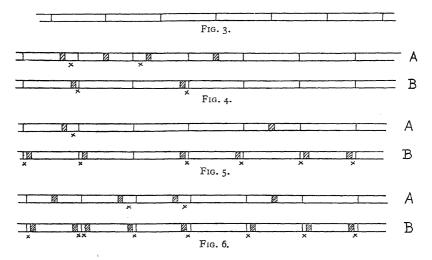
† It must be considered possible that regions of modification may also exist which do not cause micelle rupture in cuprammonium solution, but which may do so after the material has been boiled in dilute alkali.

out of the fibre. In (A) a total of approximately one-half of a micelle may pass out, while in (B) a total of only one-eighth may pass out, from among the six micelles represented in each case.

These relationships, predicted on the assumptions made, are in agreement with observation, at least for copper numbers above about 1.5.

We may now consider the case of two celluloses of the same viscosity, one degraded by the acid attack and the other by the oxidative attack. These may be represented as in Fig. 5, (A) and (B) respectively. We assume here that the six micelles in (B), from which only about one-sixteenth of a micelle has been separated in each case, will represent the conditions for a viscosity equal to that represented by the four intact micelles plus the fragments, much smaller than  $\frac{1}{16}$ , into which the other two micelles are separated by the regions of modification in A.\*

From this it would follow that (A) will have a lower copper number and a lower solubility number than (B), and this is in accordance with ob-



servation. The micelle fragments which will pass out in the solubility number determination are again indicated by crosses.

Lastly, we will consider the case of two celluloses of the same solubility number, one degraded by the acid attack and the other by the oxidative attack. These may be represented as in Fig. 6, (A) and (B) respectively. Here, in each case, the solubility number is represented by a total of half a micelle among the six micelles shown. On our assumptions, we may expect (A) to have a lower viscosity than (B) and also a lower copper number. This is again in accordance with observation.

The suggestions made show that it is possible, by the consistent use of a few simple assumptions, to interpret, in a qualitative way, the relationships under consideration. To the writer, at least, it is difficult to visualise an interpretation of these relationships on lines which differ greatly from those now suggested. It was, for example, found difficult to interpret the relationships between copper numbers and solubility

<sup>\*</sup>It is, of course, impossible actually to represent conditions which will correspond with equal viscosity, but some such relationship as that indicated must hold, on the assumptions made.

numbers of celluloses of the same viscosity, degraded by acid or by oxidation, without the assumption that in the former case the micelle fragments are more heterogeneous as regards length than in the latter case. The assumption made should be capable of being checked by experiment, as it implies that the viscosity of the cellulose dissolved out in the solubility number determination would be higher in the case of acid attack than in the case of oxidative attack. Moreover, the size distribution of the particles in the cuprammonium solutions might be compared by an ultra-filtration method or by some other means.

The interpretation of the larger loss in strength on boiling with dilute alkali of an oxidised cellulose as compared with an acid degraded cellulose presents some difficulty. It may be that the endwise affinity between micelles, or micelle fragments, is very largely destroyed by acid hydrolysis, whereas in the case of oxidative attack the endwise affinity is much greater (owing, perhaps, to considerable residual affinity between contiguous aldehydic groups). The loss in strength of oxidised celluloses on alkaline boiling might then be explained by the removal of the aldehydic components.

In conclusion, one other point related to tensile strength may be referred to. It has been observed that degraded cellulosic materials show a diminution of tensile strength on wetting.8 This might receive an explanation as being due to the lateral forcing apart of the micelles by the absorbed water. In undegraded material this may be expected to have relatively little effect on the tensile strength as the micelles are intact. In degraded material, on the other hand, the lateral union of the micelles is of relatively greater importance in respect of the tensile strength and, when this union is loosened, the weakening effect of the presence of regions of modification in the micellar chains will be more apparent.

Added at the Meeting.—The working hypothesis put forward is clearly only applicable to limited degrees of degradation. To provide for more extensive degradation it would be necessary to assume that fragments of micelles much smaller than one-quarter may be separated off by acid attack, and that fragments correspondingly smaller than one-sixteenth may be separated by oxidative attack, and further, that when one fragment has been separated from the end of a micelle by oxidative attack, further similar fragments may be successively separated off as degradation progresses.

The hypothesis may be modified to suit a conception of the fibre in which micelles of unlimited length are postulated. It would then be assumed that oxidative attack takes place so that the regions of modification are grouped more or less closely together, whereas in the case of acid attack they are more uniformly distributed along the micelles.

It should also be pointed out that it is not correct to speak of the cellulose which remains undissolved in the solubility number method as undegraded without some qualification. A material tendered by acid, with log. viscosity of 1.91, yielded a residual cellulose with log. viscosity 1.87. Further attack by atmospheric oxygen appears to have occurred during the treatment with caustic soda. The cellulose which dissolved was reprecipitated, freed from alkali and dried, and was found to have log. viscosity 2.6.

#### GENERAL DISCUSSION.

**Dr. Lonsdale** (London), in presenting the above three papers for discussion, said: Measurements made in the British Silk Research Laboratories of the transverse electrical conductivity of silk cloth removed from solutions of different hydrogen-ion concentrations, which will be described in another place, have given results in some degree parallel with those shown in the swelling curve (Fig. 1) in the paper on swelling. There are difficulties in the way of these electrical measurements and they have as yet been made only at intervals of about one  $p_{\mathbf{H}}$  unit, but in its broad aspects the curve showing the relations so far indicated by them between the  $p_{\mathbf{H}}$  value and the conductivity is somewhat similar to the swelling curve (Fig. 1); the conductivity appears to be low on the acid side of  $p_{\mathbf{H}}$  3.8 where it reaches a minimum and then to increase on the alkaline side to a comparatively high value.

Professor E. Elöd (Karlsruhe i. B.) said: I beg to point out that measurements of swellings of this kind are very uncertain. The silk fibre with its very irregular cross-sections might by turning in swelling change its position and cause wrong conclusions. Only by planimetric measurements of the cross-sections before and after swelling can exact values be obtained. On the other hand we could show (together with N. Balla) that the values of swelling resulting from the increase of weight of carefully centrifugated silk (with well-known comparative tests) shows a maximum at about  $p_{\rm H}$  1.3 and a minimum at about  $p_{\rm H}$ 5.1. Undoubtedly such measurements are more difficult with silk than with wool. I may also state that the mentioned values of the isoelectric point may not be very probable: the silk fibre consists mainly, at least in its crystallised part, of glycine (40.5 per cent.), alanine (25.5 per cent.), and tyrosine (II-O per cent.). The dissociation constants of these compounds by no means admit of such acid values of the isoelectric point as for instance, I.4 or 2.8.1

By the desamidisation of silk so that the fibre loses its tensile strength, but still shows the unchanged X-ray diagram, thus consisting chiefly of unaltered crystallites, the iso-electric point varies from about 4.0 to 4.4 at most, but never below 4.0. Also in cases of chemical destruction through alkali or acid, resulting in the dissolution into fibriles, the remainder (the crystalline part) shows a value of about 4.6. It should be emphasised that the cleaning of the fibres must be electrodialytically done between platinum electrodes in running distilled water, so that all electrolytes which disturb the measurements can be for certain eliminated.

**Dr. W. S. Denham** (Leeds) (communicated): The experimental results communicated were obtained under the conditions described in the paper, where the question of the filaments shifting during a series of observations is referred to. It is believed that the methods adopted avoid serious error due to this cause and that the minimum values observed are real for the conditions described; they were reproduced in several independent series of observations made with different sets of filaments. In their reference to isoelectric points, which is the occasion of Professor Elöd's interesting statement of his views, the authors confine themselves in the paper at this stage of an investigation,

<sup>&</sup>lt;sup>1</sup> See Hawley and Johnson, Ind. Eng. Chem., 22, 297, 1930; Shozo Bito, Bull. Seri. and Silk Ind. Japan, 4, No. 2, 1931.

which is still in progress, to pointing out merely the approximations between the  $p_{\rm H}$  values at the observed minimum swellings and the  $p_{\rm H}$  values that have been reported by different observers as defining the isoelectric point of silk.

Mr. Nodder, in putting his paper forward for discussion, added: The working hypothesis put forward is clearly only applicable to limited degrees of degradation. To provide for more extensive degradation it would be necessary to assume that fragments of micelles much smaller than one-quarter may be separated off by acid attack, and that fragments correspondingly smaller than one-sixteenth may be separated by oxidative attack, and further, that when one fragment has been separated from the end of a micelle by oxidative attack, further similar fragments may be successively separated off as degradation progresses.

The hypothesis may be modified to suit a conception of the fibre in which micelles of unlimited length are postulated. It would then be assumed that oxidative attack takes place so that the regions of modification are grouped more or less closely together, whereas in the case of acid attack they are more uniformly distributed along the micelles.

It should also be pointed out that it is not correct to speak of the cellulose which remains undissolved in the solubility number method as undegraded without some qualification. A material tendered by acid, with log. viscosity of  $\bar{\imath}$ -91, yielded a residual cellulose with log. viscosity  $\bar{\imath}$ -87. Further attack by atmospheric oxygen appears to have occurred during the treatment with caustic soda. The cellulose which dissolved was reprecipitated, freed from alkali and dried, and was found to have log. viscosity  $\bar{\imath}$ -6.

It is felt that a correct interpretation of the mode of origin of the planes of segmentation referred to in the paper will go far towards the

elucidation of fibre degradation.

#### PART III.—MANUFACTURING PROCESSES.

#### ON THE THEORY OF THE DYEING PROCESS. THE INFLUENCE OF ACID-DYES ON ANIMAL FIBRES.

By Egon Elöb.

Technische Hochschule, Karlsruhe,

Received 7th July, 1932.

Possible explanations of the processes taking place during the dyeing of protein fibres with acid-dyes, as well as of the influence of acids on protein fibres have often been discussed in the technical literature.1 The situation may appear to be so advanced through the experimental work carried out recently by us, that a comprehensive survey of the material (both that already published, and also new material) appears to be justified.

Without doubt the processes of dyeing are complicated. They consist of many partial processes. Many of the hitherto discussed and experimentally supported views are indeed applicable to separate partial processes or to special cases, but they do not, however, afford a satisfactory picture of the entire process and are not capable of exhaustive application. Various partial processes, e.g. the important rôle of the colourless acids added, the time period of taking up of colour under definite conditions, etc., have so far remained unexplained.

We shall not here give an exhaustive repetition of the literature concerned but shall refer only to some of it.

<sup>1</sup>Compare Gelmo and Suida, M., 833, 1905; M., 225, 1906. Walker and Appleyard, J. Chem. Soc., 69, 1347, 1896; 69, 1334, 1896. v. Georgie-vics, M., 709, 1894; M., 32, 1075, 1911. E. Knecht, Ber., 37, 3479, 1904. Dietl, Koll. Z., 13, 319, 1913. Vorländer and Perold, Ann., 945, 288, 1906. K. H. Meyer, and Fickentscher, M.T.B., 8, 781, 1927. Paddon, J. Physic. Chem., 33, 1107, 1929. Lottermoser, M.T.B., 11, 627, 1930. Bancroft, J. Physic. Chem., 18, 118, 1914; 19, 50, 1915; Amer. Dyestuff. Rep., 18, 148, 1929. Briggs and Bull, J. physic. Chem., 26, 845, 1922. H. Boxser, Amer. Dyestuff Rep., 21, 71, 1932. Paessler and König, Z. angew. Chem., 44, 288, 304, 1931. Elöd, Koll. Beih., 19, 320, 1925; Z. angew. Chem., 38, 199, 1925; 38, 837 and 1112, 1925; 40, 1240, 1927; Festschr. Techn. Hochschule, 490, 1925; Elöd and Pieper, Z. angew. Chem., 41, 16, 1928; Elöd and Silva, Z. physik. Chem., 137A, 142, 1928; M.T.B., 10, 707, 1929. C. C. Schmidt, Z. physik. Chem., 15, 60, 1894. W. M. Scott, C. Abtl. I, 2406, 1926; Salvaterra, M., 34, 255, 1913; J. Physic. Chem., 2, 50. Pelet-Jolivet, Die Theorie der Färbeprozesse, 1911; P. Pfeiffer and Mitarb, J. prakt. Chem. (2), 126, 97, 1930. L. M. Chappmann and Mitarb, J. biolog. Chem., 72, 707, 1927. Rawlins and Schmidt, J. Biolog. Chem., 82, 709, 1929; 88, 271, 1930. Gortner, J. Biol. Chem., 74, 409, 1927. Houch, J. physic. Chem., 32, 161, 1928.

From the work of Bancroft,<sup>2</sup> Briggs and Bull<sup>3</sup> it follows that the dyestuff anions are taken up by wool only after the latter has been positively charged by the preceding absorption of H-ions by charge-exchange or by neutralisation. On the other hand, E. Knecht<sup>4</sup> and later K. H. Meyer and H. Fickentscher<sup>5</sup> have shown that the maximum amounts (under definite conditions) of colour-acids taken up by wool, as well as by silk, comply so far with the stoichiometrically equivalent ratios, that the formation of salt-like chemical compounds between the basic groups of the wool, or the silk, and the colour-acid anions can be just as little doubted as the protein salt-formation between protein fibres and, e.g. inorganic acids, such as hydrochloric acid, etc. Moreover, in the case of skin fibres the ratios are in this respect analogous. In a recent work of A. Bravo and F. Baldracco<sup>6</sup> it is shown that also the skin fibres

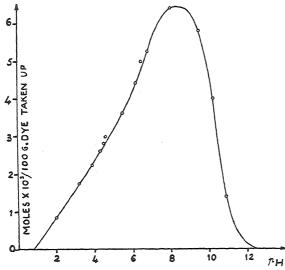


Fig. 1.—Crystal violet taken up by wool. Temp. 90° C., bath ratio 1:50, 0.6 g. dyestuff/litre.

take up the colouracids in stoichiometrically equivalent ratios.

Our attitude towards the conception of Bancroft and his colleagues will be mentioned later. Against the theory enunciated by E. Knecht as well as that by K. H. Meyer it may be remarked, that though it is indeed for decisive "chemical theory" of the dyeing in question, nevertheless it by no means sufficiently solves the problem. Under practical

conditions of dyeing the maximum possible amount of dyestuff or acid is never taken up. Since, on the other hand, this explanation is silent also as to the course of the dyeing process, and since various observations have been submitted which make a further investigation into the details or minutiæ of such a process seem indubitably essential, a comprehensive programme of work has been carried out. During this work I have had the able assistance of Dr.-Ing. E. Pieper, Dipl.-Ing. G. Chr. Vogel, Dipl.-Ing. A. Köhnlein and especially of Dr.-Ing. E. Silva and Dr.-Ing. F. Böhme.

In the dyeing of degummed natural silk we first found that by decreasing the  $p_{\rm H}$  values in the dyeing bath the amount of bound colouracid (which, by the way, was far below the amount necessary to saturate the silk with dyestuff) passes through a maximum. This observation

<sup>&</sup>lt;sup>2</sup> J. Physic. Chem., 18, 118, 1914; 19, 50, 1915; Amer. Dyestuff Rep., 18, 148, 1929.

<sup>&</sup>lt;sup>3</sup> J. Physic. Chem., 26, 845, 1922. <sup>5</sup> MTB, 8, 781, 1927.

<sup>&</sup>lt;sup>4</sup> Ber., **37**, 3479, 1904. <sup>6</sup> Collegium, 338, 1932.

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was incompatible with the theory of Briggs and Bull. It would have been reasonable to assume that in the region of higher hydrogen ion concentration, flocculation would take place, and that this would change the particle-size, as is the case with basic dyestuffs in the region of higher hydrogen ion concentration. As an example, the dependence of the taking up of colour (crystal violet) by wool at 90° C. upon the  $p_{\rm H}$  values of the dyestuff solution is shown in Fig. 1. The re-entrant branch of the curve is traceable to the evident enlargement of particles of the basic dyestuff in the alkaline region.

Since, however, the same phenomenon of maxima appears not only in very highly diluted solutions of those dyestuffs which show no flocculation (established by application of the Tyndall Effect), but also in pure crystalloid solutions (e.g. by the simultaneous influence of chromic acid

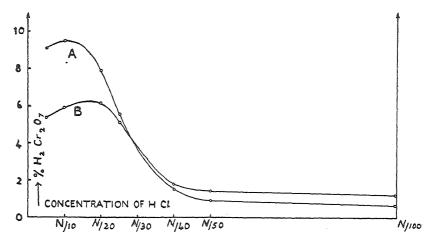


Fig. 2.—Simultaneous influence of chromic acid and hydrochloric acid on wool and skin.

A, wool.

B, skin.

and hydrochloric acid on wool, as well as on hides, where there can be no question of colloidal flocculation or of the changing of particle-size—comp. Fig. 2—A. Köhnlein), this question has been more closely investigated by Dr.-Ing. Silva. It appears that in the systems under discussion (fibre protein + acid), the conditions which are necessary for the appearance of Donnan membrane equilibrium 7 have been fulfilled. In such systems there prevails a complete equilibrium between the fibre-protein and acid; on the other hand, however, ions are held back in the solid phase.

## Fibre protein - Acid - Water.

The proof of the establishment of a definite state of equilibrium between the fibre-protein and the acid (leaving out of consideration the absorption-equilibria—which, however, constitute only a partial process), was until quite recently not to be found in the literature. An

exact equilibrium cannot indeed be expected in such systems in all cases, since the fibre protein on treatment with acids changes chemically and is partly disintegrated. By observation of definite precautions, however, a complete equilibrium can be reached.

For the study of the equilibrium ratio, after adjustment of the re-

spective final states on both sides of the equation:

Fibre-protein + acid = protein salt + water

the following criteria were ascertained:-

(a) The H ion and Cl ion concentrations within the protein gel.

(b) The ion concentrations in the bath, which were in equilibrium with fibre protein, and

(c) The corresponding degree of swelling of the fibre-protein in the

final state.

The experiments were carried out as follows:-

I. A fibre sample of known weight was treated with n c.c. of acid solution with careful shaking so long as no change in the bath was observed. From the  $p_{\rm H}$  values of the solution before and after the treatment, the bath ratio, the degree of swelling, and the Cl ion concentration within the gel can be calculated. The  $p_{\rm Cl}$  values in the solution before and after the treatment complete the measurements. The degree of swelling of the protein fibre was ascertained by the increase in weight which was observed after it had been whirled in an electric centrifuge with samples of known degree of swelling.

2. The fibre samples containing the resulting protein salts were introduced into conductivity water and shaken carefully at intervals until a constant end point was reached. The above mentioned measurements were then repeated. (Compare E. Elöd and E. Silva, Z. physik. Chem.,

137A, 141, 1928.

In order to show that the amounts of acid taken up by protein fibres are dependent only upon the final  $p_{\rm H}$  value of the dye bath, several measurements were carried out with varying bath ratios. (I:20, I:40, I:100, I:200). It was shown that the values so obtained all lie upon the same curve as that obtained at the same  $p_{\rm H}$  value but with the bath ratio I:20. Thus it is possible, for example, to calculate the Cl ion concentration in the protein gel at equilibrium for any bath ratio whatsoever, by reference only of end  $p_{\rm H}$  values. In the case of wool as well as of hides, there appears the phenomenon (which has also been observed in other cases—e.g. with other proteins), that by working under conditions at which acid decomposition of proteins was avoided (e.g. at room temperature), there is obtained an end point for the capacity of acid combination; in the case of hides at the  $p_{\rm H}$  value of about I·19, in case of wool at the  $p_{\rm H}$  value of I·3.

Notwithstanding, the influence of acids on fibre protein is doubtless not a simple relationship, on account of the more or less specific properties of the anions, as is shown in Tables I.-VI. and curves 3 and 4, which compare the amount of sulphuric acid or picric acid taken up by wool

with that of hydrochloric acid taken up.

The experiments carried out at 20° C. over a period of about three days, with hydrochloric acid or sulphuric acid and wool, showed the existence of an equilibrium. As can be seen from Fig. 3, at the same final

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 $p_{\rm H}$  values of the bath larger amounts of sulphuric acid than of hydrochloric acid enter into combination. This phenomenon can, however, be

observed only between the isoelectric point of the wool  $(p_{\rm H}=4.9)$  and a  $p_{\rm H}$  value of about 2.4. An explanation of this can be sought in the known slight solubility of the resulting protein sulphates. There is another explanation, but we will defer consideration of this for the present. Nevertheless it is interesting to note that from a  $p_{\rm H}$  value of 2.4 to about 4.8 wool takes up twice as many equivalents of sulphuric acid as of hydrochloric acid.

If the wool samples which have entered into combination with sulphuric acid are treated with conductivity water, the sulphuric acid is

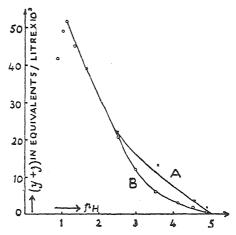


Fig. 3.—The acid combination capacity of wool.

(Temp. 20° C.). System: Wool—Sulphuric acid—Water.

A, Sulphuric acid. B, Hydrochloric acid.

liberated and a state of equilibrium is produced. By calculation of the sulphate ion concentration in the wool gel (with the help of original sulphate ion concentration of protein sulphate in the wool and of the degree of swelling) it may be shown that, at the same final values of H-ion concentration, the amount of sulphate present in the wool is the same as in the case of taking up sulphuric acid (Table IV.). The ratios also are similar for the influence of hydrochloric acid on wool, etc. (Table III.).

TABLE I.—WOOL—HYDROCHLORIC ACID—WATER (TEMP. 20° C.).

	Protein + Hydrochloric Acid.							
Exper. No.	$p_{\mathrm{H}}$ Value	of Bath.	Degree of		(y+z) in mol./litre.			
	Before.	After.	Swelling.	x in mol./litre.				
1 2 3 4 5 6 7 8 9 10	0·80 0·88 0·96 1·05 1·73 2·04 2·34 2·61 2·91 3·21 3·49	0.88 1.02 1.13 1.35 2.51 2.98 3.52 4.12 4.52 4.90 4.91	1·538 1·544 1·552 1·566 1·501 1·491 1·491 1·486 1·473 1·468 1·473	0·138 0·99 × 10 <sup>-1</sup> 0·80 × 10 <sup>-1</sup> 0·47 × 10 <sup>-1</sup> 0·32 × 10 <sup>-2</sup> 0·11 × 10 <sup>-2</sup> 0·30 × 10 <sup>-3</sup> 0·76 × 10 <sup>-4</sup> 0·13 × 10 <sup>-4</sup> 0·12 × 10 <sup>-4</sup>	0·416 0·492 0·515 0·448 0·205 0·120 0·060 0·032 0·017 0·008 0·004			

x= concentration of H-ions or Cl-ions (mol./litre) in the bath. (y+z)= concentration of Cl-ions (mol./litre) in the gel of the wool in the state of equilibrium.

TABLE II.—WOOL—SULPHURIC ACID—WATER (TEMP. 20° C.).

#### Protein + Sulphuric Acid.

p <sub>H</sub> Value of Bath.		Degree of	1,00	(v+z) in	
Before.	After.	Swelling.	x in mol./litre.	mol./litre.	
0.97	1.08	1.517	0.129	0.65	
1.38	1.67	1.525	0.30 × 10-1	0.39	
1.67	2.50	1.508	0.32 × 10-2	0.22	
2.04	3.58	1.506	0.26 × 10-3	0.13	
2.26	4.05	1.497	0.89 × 10-4	0.072	
2.56	4.56	1.484	0.28 × 10-4	0.036	
2.86	4.96	1.505	0.11 × 10-4	0.018	
3.17	4.92	1.491	0·12 × 10 <sup>-4</sup>	0.009	
3.24	4.97	1.480	0.10 × 10-4	0.004	

x= concentration of the H-ions of sulphate ions in equiv./litre in the bath. (y+z)= concentration of the sulphate ions in equiv./litre in wool gel after attainment of equilibrium.

TABLE III.—WOOL—HYDROCHLORIC ACID—WATER (TEMP. 20° C.).

Protein Chloride + Water.						
b <sub>H</sub> Value of Bath.	Degree of Swelling.	π in mol./litre.	(y+z) in mol./litre			
1.89	1.23	0.13 × 10-1	0.25			
1.00	1.520	0·13 × 10 <sup>-1</sup>	0.33			
1.93	1.222	0·12 × 10 <sup>-1</sup>	0.37			
1.96	1.529	0.11 × 10-1	0.35			
2.70	1.495	$0.20 \times 10^{-2}$	0.18			
3.04	1.490	$0.91 \times 10_{-3}$	0.11			
3.43	1.495	$0.37 \times 10^{-3}$	0.055			
3.84	1.489	$0.14 \times 10^{-3}$	0.032			
4.35	1.480	0.45 × 10-4	0.017			
4.90	1.468	0·13 × 10-4	0.008			

TABLE IV.—Wool—Sulphuric Acid—Water (Temp. 20° C.).

Protein Sulphate + Water.					
p <sub>H</sub> Value of Bath.	Degree of Swelling.	x in mol./litre.	(y+z) in mol./litre		
2.06	1.498	0·10 × 10-1	0.2		
2.18	1.490	0.76 × 10-3	0.30		
2.22	1.489	$0.28 \times 10^{-2}$	0.10		
3.36	1.491	$0.44 \times 10^{-3}$	0.13		
4.31	1.461	$0.62 \times 10^{-4}$	0.072		
4.21	1.478	$0.31 \times 10^{-4}$	0.036		
4.82	1.466	$0.15 \times 10^{-4}$	0.018		
4.82	1.463	$0.15 \times 10^{-4}$	0.009		
5.07	1.453	0.09 × 10-4	0.004		

#### TABLE V.-Wool-Picric Acid-Water.

Protein + Picric Acid.

		11010111   110110 11010		
alu	e of Bath.	Degree of	x in mol./litre.	(y+z) in
	After.	Swelling.		mol./litre.
	2·19	I·573 I·547	0.65 × 10 <sup>-2</sup> 0.49 × 10 <sup>-3</sup>	0·46 0·27

$p_{ m H}$ Value of Bath.		Degree of	x in mol./litre.	(y+z) in
Before.	After.	Swelling.		mol./litre.
I·37 I·67	2·19 3·31	1·573 1·547	0.65 × 10 <sup>-2</sup> 0.49 × 10 <sup>-3</sup>	0·46 0·27
1·94 2·22	3.91	1.537	0·12 × 10 <sup>-3</sup> 0·48 × 10 <sup>-4</sup>	0·15 0·077
2.53	4·32 4·77	1·523 1·491	0·17 × 10-4	0.041
2.84	5.18	1.525	0.66 × 10-5	0.019

x = concentration of H-ions (mol./litre) in the bath.

(y + z) =concentration of picrate ions (equiv./litre) in wool gel after attainment of equilibrium.

TABLE VI.-WOOL-PICRIC ACID-WATER.

Protein Picrate + Water.					
p <sub>H</sub> Value of Bath.	Degree of Swelling.	x in mol./litre.	(y+z) in mol./litre.		
2·61 3·41 3·87 4·27 4·59 4·96	1·574 1·556 1·551 1·530 1·502 1·514	0·25 × 10 <sup>-2</sup> 0·39 × 10 <sup>-3</sup> 0·14 × 10 <sup>-3</sup> 0·54 × 10 <sup>-4</sup> 0·26 × 10 <sup>-4</sup> 0·11 × 10 <sup>-4</sup>	0.43 0.26 0.15 0.080 0.040 0.019		

In the case of similar molecular dispersions of picric acid, experiments gave the results shown in Fig. 4 (F. Böhme) and in Tables V. and VI. Though picric acid has been an object of repeated investigation, it appeared interesting in this connection to test anew the question of its being taken up by wool. As may be seen, at the same initial  $p_H$  values of the bath, wool binds considerably larger amounts of picric acid than of hydrochloric acid. With increasing acidity of the bath, however, this difference gradually diminishes. It appears as if in the region of higher H-ion concentration more of the acid character comes into play, and in the lower concentration more of that which we may call the dyestuff character. In passing, it is interesting to note that in following the time ratio of acid combination with wool, hydrochloric acid is taken up at the same velocity as picric acid at the initial  $p_{\rm H}$  values of the bath, e.g. 1.37, whereas at higher  $p_{\rm H}$  values, e.g. 2.25, the velocity of picric acid absorption is considerably greater than that of hydrochloric acid (Fig. 5, F. Böhme). These questions will be considered later.

Even the protein picrates liberate picric acid in conductivity water (Table VI.). The equilibria referred to the same final  $p_{\rm H}$  values of the bath correspond to those which are reached in the case of the taking up of picric acid. Walker and Appleyard, on other experimental

evidence, have already referred to the appearance of equilibria in this system.

On the strength of the relations obtained through the influence of acids on fibre protein, we sought an insight into the processes which take

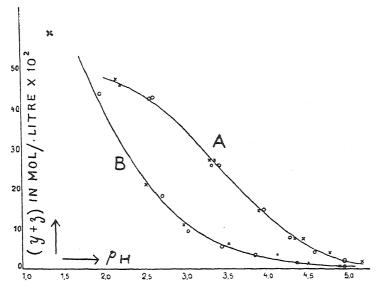


Fig. 4.—The acid combination capacity of wool. Temp. 20° C. System: wool—picric acid—water.

A, Picric acid. B, Hydrochloric acid.

place during the dyeing of wool, natural silk, and hides, with acid dyes in relation to the  $p_{\rm H}$  values of the dyeing bath (in the presence of added colourless acids).

#### Fibre protein - Acid Dye and Acid - Water.

Since the necessary conditions for the application of the relationship as to the distribution of diffusible ions (as given by the Donnan membrane equilibrium) were fulfilled for the influence of acids on fibre protein, and since their application to the determination of the swelling equilibria has proved to be correct, the next conclusion was to test the correctness of the relationships already suspected. Since according to the relations

$$\frac{[H']_a}{[H']_i} = \frac{[\text{anion}]_i}{[\text{anion}]_a} = 1 + \frac{c_1}{c_2 + c_3} = \lambda$$

(where  $[H^*]_a$  is the H-ion concentration of the bath and  $[H^*]_i$ , the H-ion concentration of the wool, etc.), and since the relationship of the concentration of the colour-acid anions in the wool  $[Da']_i$  to those in the bath

$$[Da']_a$$
, i.e.  $\lambda = \frac{[\text{colour acid anions}]_i}{[\text{colour acid anions}]_a}$  must hold good, it is easy to cal-

culate, from the values obtained through the equation  $\lambda = I + \frac{c_1}{c_2 + c_3}$ 

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the distribution of colour-acid anions in the protein gel as well as in the bath. From this  $c_1$  is the H ion concentration in the protein gel, and  $c_2$  the H-ion concentration in the bath, the values of which are taken from Table I. (protein + hydrochloric acid). For  $c_3$ , i.e. the concentration of the colour acid anions, we select the two experimentally tested

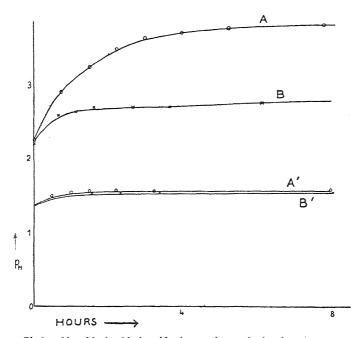


Fig. 5.—Picric acid and hydrochloric acid taken up by wool related to time at the initial  $p_{\rm H}$  values of 1.37 and 2.25.

A, A', Picric acid.

B, B', Hydrochloric acid.

values, namely, 0.002 mol./litre and 0.016 mol./litre respectively, for the illustrative calculation given below. It is thus possible to calculate the values stated in Table VII. The following deductions can be made:—

- (I) The values for  $\lambda = \frac{[Da']_a}{[Da']_i}$  pass through a maximum.
- (2) This maximum will be reached in stronger acidic regions, with increasing dye concentration, in which case
- (3) The proportion of colour-acid taken up by the protein will grow smaller, though not in direct relation to the increase of dye concentration (in Table VII. the dyestuff concentration rises to eight times as much in the third column, whereas the  $\lambda$  values fall to nearly one-third at a maximum thus showing a higher dyestuff absorption, though not corresponding to one-eighth).

The amount of dyestuff bound by the fibre protein at a maximum in each case is dependent upon the choice of experimental conditions, and thus upon the final  $p_{\rm H}$  value of the bath, upon the concentration of the dyestuff and obviously upon the nature of the dye.

The results found experimentally (E. Pieper) on the dyeing of natural silk with acid dyes thus stand in close harmony with the theoretical requirements (E. Silva).

We have to imagine the process of dyeing fibre protein with acid dyes in acid bath to be thus: The colourless acid, on account of its greater diffusibility, penetrates the protein before the colour-acid and forms the corresponding protein salt. With the appearance of protein salt the membrane action of the fibre protein comes into play and causes unequal distribution of the colour anions between the fibre and the bath, according to the ratio  $\lambda$ , i.e. the colour anions distribute themselves in the same ratio as those of the colourless acid. Thus the formation of the protein salt with the colourless acid appears to be the primary process which is followed by the taking up of the dyestuff as a secondary process. The time difference (required by the theory) in the velocity of formation of the two types of protein salts (with the colourless and the colour acids) should be experimentally determinable. Since the

	$c_3 = 0.002 \text{ mol./litre.}$	$c_3 =  ext{o}$ or or 6 mol./litre.	
Exper. No.	$\mathbf{r} + \frac{c_1}{c_2 + c_3} = \frac{[Da']_i}{[Da']_a}.$	$1 + \frac{c_1}{c_2 + c_3} = \frac{[Da']_i}{[Da']_a}.$	
ī	4.0	4.74	
3	4·5 7·1	4.93 6.1	
	12.9	10.2	
4 5 6	42.2	12.0	
6	35.5	7*3	
7 8	27.0	4.7	
	12.4	2.9	
9	7 <b>·</b> 9 4·8	2.0	
10		1.5	
II	<b>2</b> *9	1.3	

TABLE VII.

velocity of protein salt formation at higher temperatures is so great that it cannot readily be followed experimentally, we worked at lower temperatures, *i.e.* at 20° and 50° C. (F. Böhme and A. Köhnlein). Contrary to other views, experiments carried out at the above-mentioned temperatures, which obviously required correspondingly longer experimental time (at 20° about 8 days and at 50° about twenty-four hours), showed genuine properties of a usual character throughout. From experiments of this type, it is therefore possible to draw binding conclusions for practical relationships.

We thus succeeded in evaluating the relatively slow taking up of colour anions and the rapid formation of protein salts with the added acid (hydrochloric acid) as independent processes, separable in time, thereby proving the validity of the above assumption.

Crystal ponceau 6R, thiocarmine B and sulphorhodamine R were used as dyestuffs. The change in concentration of H-ions was determined potentiometrically (with the quinhydrone—or the hydrogen electrodes),—that of the dye colorometrically (in some cases by titration with TiCl<sub>2</sub>).

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The ratios were determined for various initial values of the H-ion concentration of the solution. As an example we give here Fig. 6

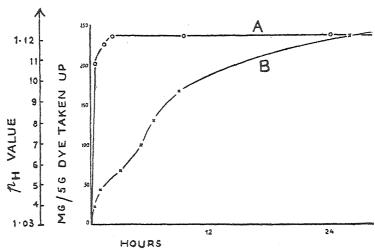


Fig. 6.—Course of the dyeing of wool with Crystal Ponceau (5 per cent. dyestuff, bath ratio 1:50, Temp. 20° C., initial  $p_{\rm H}=1$ ).

A,  $p_{\rm H}$ .

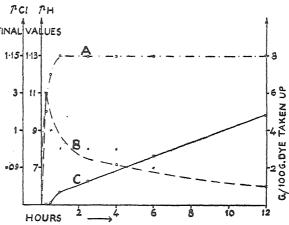
B, Dyestuff taken up.

(F. Böhme), which shows the course of dyeing in hydrochloric acid solution with crystal ponceau and wool. As may be seen, an energetic acid absorption takes place at 20° C. under these conditions (also at the

various initial  $p_{\mathbf{H}}$  values which have been experimentally tested) within a very short time (half an hour); at this time the absorption is practically complete and it rises only very slightly afterwards. The colour absorption, on the contrary, occurs remarkably as is the beginning (in

the first half hour

only a very small



quite evident in Fig. 7.—Course of the dyeing of wool with Crystal Ponceau and the beginning (in the change of  $p_{Cl}$ . Temp. 20° C., bath ratio 1:50, 5 per cent.

A,  $p_{\mathbf{H}}$ . B,  $p_{\mathbf{Cl}}$ . C, Dyestuff taken up.

portion of the dye disappears from the solution). Thus, we are concerned clearly with two separate processes.

Moreover it was to be expected that the curves for the  $p_{Cl}$  values would show a tendency contrary to that of the colour absorption, through the

substitution of Cl-ion (taken up by fibre protein in the primary process) by colour anions, as a gradual secondary process. It is further to be

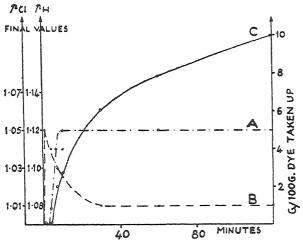


Fig. 8.—Course of the dyeing of wool with Crystal Ponceau and stances the change of  $p_{Cl}$ . Temp. 50° C., bath ratio 1:50. B, p<sub>Cl</sub>. A,  $p_{\rm H}$ . C, Dyestuff taken up.

expected that (primarily due to the distribution of ions eventually due to the slight solubility of the compounds formed by the reaction of protein with colour acid), quantitative, well time, as differences will present themselves according to the nature of the dyestuff. The circumare

clearly shown in and 8 Figs. 7

The displacement of Cl-ions occurs also in the case of a subsequent or additional dyeing of an already dyed wool, and is experimentally determinable as shown in Fig. 9.

The absolute velocities of colour absorption are, at the same tem-

perature, obviously dependent upon the nature of the dyestuff, its difvelocity, fusion the nature of the fibre used etc. The general conception obtained experimentally in various cases was always analogous. We found the same ratios with other protein fibres, e.g. hides. We shall report on this elsewhere.

(A. Köhnlein).

The taking up of colourless acids (hydrochloric acid) has, as may especially emphasised, always been independent of the nature and amount of the dyestuff. This clearly de-

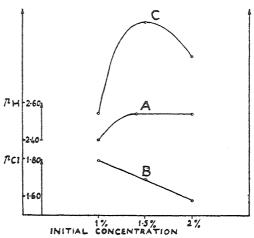


Fig. 9.—Displacement of Cl-ions through additional dveing of already dyed wool. A, p<sub>H</sub>. B, p<sub>Cl</sub>. C, Dyestuff taken up.

monstrates the correctness of the assumption of the primary formation of a protein salt.

The taking up of the colour in each case shows, in the initial time

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period, a regularly appearing peculiarity which is apparently set up rapidly at the beginning (adsorption?) but soon undergoes an evident diminution, the cause of which cannot as yet be ascertained.

## The Appearance of a Maximum of Colour-Acid Combination.

A maximum of the colour acid combination appears with increasing H-ion concentration. This phenomenon, in the case of dyestuffs by which changes in dispersivity are almost impossible or at least improbable, contradicts the above-mentioned view of Bancroft, which attributes colour absorption to the exchange of charges, since according to this view, with increasing acid concentration, an increasing colouracid absorption is to be expected, and this colour absorption may at the most reach a final value but can never decrease again.

Such a maximum was, however, to be expected from the above considerations. As is known, wool, for example, at room temperature

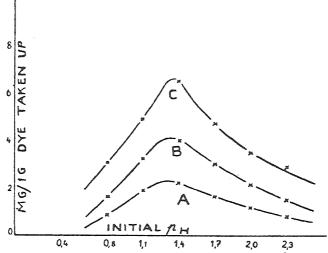


Fig. 10.—Velocity of the taking up of dyestuff in dependence upon the H-ion concentration in the bath. (r per cent. sulphorhodamin B, bath ratio r: 100, Temp. 20° C.).

A, r hour. B, 2 hours. C, 4 hours.

attains the maximum end value of the acid combination at a  $p_{\rm H}$  value of about 1·3 and remains practically constant with increasing H-ion concentration, in so far as no decomposition of the protein substance takes place. Therefore with increasing H-ion concentration of the dye bath, the expression for  $\lambda = 1 + \frac{c_1}{c_2 + c_3}$  will gradually decrease, since the values for  $c_2$  increase, those of  $c_1$  and  $c_3$ , on the other hand, remain constant.

Experiments were carried out with highly diluted dyestuffs solutions of various concentrations with dyestuffs of different constitution at 20° and 50° C., at various known  $p_{\rm H}$  values, and avoiding variation in the degree of dispersivity. They showed that not only a maximum of the quantity of combined dyestuff but also a maximum of the rate of combination appeared, corresponding to the conception that the above expression for  $\lambda$  also represents a measure of the tendency for colour

anions to diffuse into the fibre or of the diffusion potential (Fig. 10). The maximum of the rate of absorption is situated for wool at room temperature, approximately at  $p_{\rm H}=1\cdot3$ , i.e. at that point where the quantity of the combined dyestuff is also a maximum. At higher temperatures the position of the maximum is probably displaced, without causing the phenomenon itself to disappear.

#### Capacity of Acid Combination of Dyed Wool.

In addition to the investigation into the course of the combination of the dyestuff with the fibre protein, it appeared to be of interest to test the properties of dyed fibres. Thus, the determination of the capacity of acid combination of dyed wool has made it possible to follow quantitatively the chemical change occurring, in the case of wool substance,

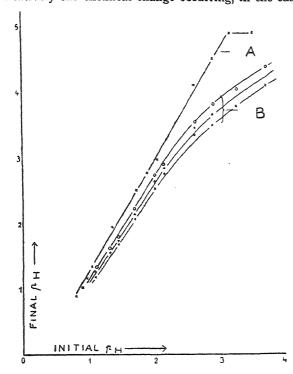


Fig. 11.—Acid combination capacity of dyed wool at 20° C. System: wool—hydrochloric acid—water.

O wool dyed with 2'5 per cent. Crystal Ponceau.

+ ", ", 5'0 ", " ", ",

X, Undyed wool. B, Dyed wool.

on account of the combination of the dye with the wool (salt formation with the colour-acid). If the taking up of the dyestuff were physical process, the chemical properties of the wool would probably experience change. wool would have to behave with acids with which it chemicombinescally this is beyond doubt to-day-exactly in the same way in the dyed state as in the undyed (provided that the dyes themselves do not combine with acids). If, however, coloration of wool with colouracids represents a formation of protein salts, which arise through neutralisation of basic groups of the wool proteins by

colour-acids, then the further capacity for acid combination of the wool, which is also conditioned by its basic groups, must be decreased, and indeed to a degree corresponding to the preceding combination with the colour-acid.

For the experiments undertaken in this direction, it was of importance to free the wool samples from diffusible electrolytes (in order to dispose E. ELÖD 341

of eventually disturbing electrolytic action) and to test the dyed pure material thus obtained for its capacity for acid combination. The removal of electrolytes was performed electrodialytically,8 in which case, for instance, wools dyed with crystal ponceau kept their dyestuff content practically undiminished. The wools were treated with crystal ponceau solutions of various concentrations (2.5, 5 and 10 per cent. dvestuff referred to the fibre weight) at an initial  $p_{\rm H}$  value of 1.3 up to complete saturation with the dyestuff at temperatures of 20° and 45° C. respectively. Following this, the dyed wool was electrodialysed at room temperature between platinum electrodes in running distilled water for several hours, until complete freedom from electrolytes was obtained. Thereupon, samples of known dry weight were inserted in hydrochloric acid solution of known concentration in the I: 20 dye bath, and the quantity of hydrochloric acid taken up the wool was potentiometrically determined. As may be seen from Fig. 11 (F. Böhme) the acid combination of the dyed wools is clearly smaller than that of the undyed. It decreases with increasing loading of the wools with the dye. The absolute quantities of acid uniting with the fibre may be calculated from the  $p_{\rm H}$  values of the solutions and the degree of swelling of the wool. These values are given in Table VIII. for some cases. From this it results,

TABLE VIII .- ACID COMBINATION OF DYED WOOL.

Degree of Swelling.	z in mol./litre.	(y+z) in mol./litre.
Swelling.	z m moi.jntie.	mol./litre.
1.57 1.57 1.57 1.57 1.49 1.49 1.49 1.47 1.47	0.45 × 10 <sup>-1</sup> 0.50 × 10 <sup>-1</sup> 0.50 × 10 <sup>-1</sup> 0.65 × 10 <sup>-1</sup> 0.71 × 10 <sup>-1</sup> 0.11 × 10 <sup>-2</sup> 0.16 × 10 <sup>-2</sup> 0.20 × 10 <sup>-2</sup> 0.27 × 10 <sup>-2</sup> 0.30 × 10 <sup>-4</sup> 0.15 × 10 <sup>-3</sup> 0.22 × 10 <sup>-3</sup>	0.56 0.50 0.42 0.23 0.107 0.100 0.094 0.085 0.0160 0.0151 0.0142 0.0128
	1·49 1·49 1·47 1·47	1·49 0·20 × 10 <sup>-2</sup> 1·49 0·27 × 10 <sup>-2</sup> 1·47 0·30 × 10 <sup>-4</sup> 1·47 0·15 × 10 <sup>-3</sup> 1·47 0·22 × 10 <sup>-3</sup>

for instance, that in the case of a wool dyed with 2.5 per cent. crystal ponceau, the quantity of acid combined is smaller by a definite amount in comparison with the undyed wool. A proportionality seems to exist between the quantity of combined acid and the decrease in the capacity for acid combination of the dyed wool. Thus, the decrease in the capacity for acid combination of a wool dyed with 10 per cent. crystal ponceau in comparison with the undyed wool amounts to 0.33, 0.022, and 0.0032 mols./litre with the corresponding initial  $p_{\rm H}$  values of the baths of 1.05, 2.04 and 2.90. On the assumption of a proportionality between the quantity of the acid uniting with the wool and the decrease of the acid combination capacity, it is to be expected that, with the same initial

<sup>8</sup> Collegium, 135, 1932.

 $p_{\rm H}$  values of the baths, the wools loaded with only one-fourth, *i.e.* 2.5 per cent. dye, would show decreases in acid combination capacity, amounting to only one-fourth of the above, *i.e.* about 0.08, 0.006 and 0.0008 mols./litre, which, considering the experimental errors, are in sufficient agreement. The corresponding values are 0.06, 0.007 and

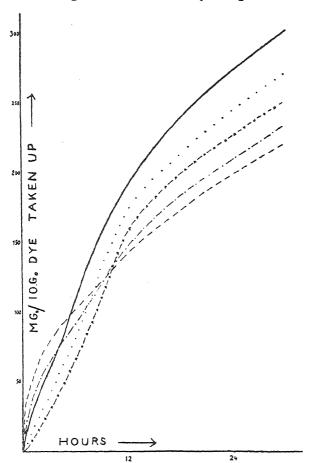


Fig. 12.—Effect of the addition of a neutral salt on the taking pairs. up of dyestuff (5 per cent. Crystal Ponceau, bath ratio 1:50, the ratemp. 20° C., initial  $p_{\rm H}=2$ ).

Dyeing without addition of salt-

Dyeing with the addition of salt 1 (per cent. Na<sub>2</sub>SO<sub>4</sub> based on fibre  $\begin{cases} 2.5 \text{ per cent.} & \dots \\ 5.0 & \dots \\ 10.0 & \dots \end{cases}$  weight)

0.0009 mol./litre. From this result the conclusion may be drawn that, under the experigiven mental conditions, the absorption of the dyestuff represents chiefly chemical process in which, for the combination both of the acid dye and of the colourless acids, basic reactive of the groups wool come into play.

# Influence of Neutral Admixtures on the Dyestuff Absorption.

According to the Donnan membrane theory the repeatedly mentioned value of  $\lambda$ is decreased by the presence of additional ion Thereby the rate at which dyestuff is taken up is influenced on account of the decrease of the diffusion poten-

tial, and it is to be expected that sufficiently large admixtures of neutral salts would change the velocity of dyeing.

Wool samples were dyed in the bath ratio of 1:50 with 5 per cent. crystal ponceau (referred to fibre weight) in the presence of 0, 2.5, 5.0, 10.0, and 15.0 per cent. sodium sulphate (likewise referred to fibre

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weight) at 20° C. and an initial  $p_{\rm H}$  value of the solutions of 2.0. Fig. 12 shows the quantity of the dyestuff taken up per unit of time. This decreases with an increase in the concentration of sodium sulphate in the bath. The previously inexplicable equalising action of the admixture of neutral salts to the dye solutions, which are of importance in practice, may also be accordingly explained.

The dyestuffs themselves play a rôle similar to that of the neutral salts if they are employed in higher concentrations. Whilst up to a certain concentration the quantity of the dye absorbed by the wool per unit of time increases with further increase of the concentration, a maximum, and then a decrease in the rate of taking up of the dyestuff is attained (cf. Fig. 13, F. Böhme). It is probably not yet possible to comprehend the

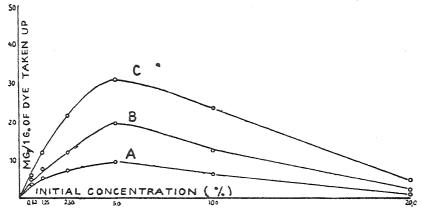


Fig. 13.—Velocity of taking up of dyestuff in dependence upon the dyestuff concentration in the bath (Crystal Ponceau 6R, bath ratio 1:50, temp. 18° C., initial  $p_{\rm H}=2$ ).

A, 1 hour.

B, 4 hours.

C, 24 hours.

relationships sufficiently thoroughly in a quantitative manner; they result, however, qualitatively, from the meaning of the value

$$\lambda = 1 + \frac{c_1}{c_2 + c_3}$$

In this case  $c_1$  and  $c_2$  have the same meaning as above,  $c_3$  is the concentration of the dyestuff in the bath. It is evident that with increasing  $c_3$   $\lambda$  decreases, at least above definite  $c_3$  values. More exact considerations may be reserved for a later communication.

#### Conclusions.

Even though far-reaching regularities result from the above-sketched theory, it must always be especially emphasised that the process of dyeing may undergo such complications, through various factors (partial processes), that one is not in a position to attack the problem exhaustively in a quantitative manner. In order to obtain an insight into the complicated relationships of such processes, it may be said here that the taking up of simple inorganic anions by the fibre proteins shows a more or less specific course. For the same initial concentrations nitrate ions, for example, are taken up by wool to a considerably higher degree than Cl-ions. This is also true of Br-ions, where, however, the difference

between the absorption of Cl-ions and Br-ions is less than that between Cl-ions and nitrate ions. Pelet-Jolivet <sup>9</sup> has already referred to the specific properties of ions in this respect.

It can, nevertheless, be said on the basis of the results quoted above, that the interpretations of the dyeing processes in question show, by a consideration of the membrane equilibrium, a course which corresponds with theoretical requirements. The experiments up to the present have for simplicity been undertaken with hydrochloric acid, which is used technically only in secondary amounts. However, from the experiments reported above there exist no grounds for doubting that we may safely extend these reflections, for instance, to sulphuric acid.

In spite of these results, which have been checked many times, and which demonstrate the decisive rôle of chemical processes in dyeing as discussed above, there have appeared contrary conceptions in the most recent literature. An ever-recurring argument against the chemical conception is based on a phase theory treatment of the dyeing processes. From the non-existence of breaks in the curves (which in heterogeneous systems are characteristic of the formation of chemical compounds), and from the general course of the curves, it is concluded that absorption alone controls the process. It may be remarked, above all, that the facts are against such conclusions, that the taking up of acids by the wool can lead first from a definite  $p_H$  value to a complete saturation of the basic valencies and thus to the maximum expected value for the absorption of the dyestuff. Below this  $p_{\mathbf{H}}$  value the basic valencies are either not activated or are in general not yet present as such. appearance of breaks can arise only after the saturation capacity of the chosen  $p_{\rm H}$  values of the dyestuff solutions has been exceeded. reaction capacity of the fibre proteins is not absolutely constant, but varies according to the acidity of the systems. This can easily be shown as follows: If, for example, wool is treated with solutions of dyestuffs of the same concentrations and of the same  $p_{\rm H}$  values, but in an increasing bath ratio, the wool, despite a surplus, does not take up any more dyestuff (Köhnlein). Only after changing the pH values of the dyebaths is it possible to vary also the amount of the dyestuff taken up. However, in this case too, the amount entering into combination, even with a considerable surplus of free acid dyes, becomes constant again for this new pH value. Accordingly the evaluation of the free amino-groups (van Slyke) in the wool, silk and other protein fibres can only be of interest if the acidity  $(p_H)$  of the diazotizing solution is fixed by measurement. Probably the amount of the really free amino-groups in the fibre proteins is only slight; they only become free and capable of reaction by acidification of the solutions, a process in which the cross linkages very probably play a part. When using amido-cellulose the conditions are, however, different. In this case there is no corresponding dependence of the combination capacity upon the amino-groups present, because with these materials the amino-groups are really free and reactive. Experimental work on these points will be reported in a future publication.

By working at room temperature the stage at which the maximum of acid is taken up is obtainable without a change in the wool substance and accordingly a break in the curve representing acid absorption can be verified. At higher temperatures and in the region of higher H-ion concentrations, the wool substance itself is chemically changed, so that the

<sup>&</sup>lt;sup>2</sup> Theorie der Färbeprozesse, 77, 1911.

non-existence of breaks in the curve appears intelligible. Before all, however, it must not be forgotten that, as was shown above, the dyeing processes are so complicated by intermingled partial processes that a phase theory explanation of such processes must seem incompatible with theoretical reasoning.

I am greatly indebted to the Karlsruher Hochschulvereinigung as well as to the Notgemeinschaft der Deutschen Wissenschaft for their

kindness in giving me means for our investigations.

### GENERAL DISCUSSION.

**Dr. Speakman** (*Leeds*) said: If Professor Elöd's exhaustive application of the Donnan theory of membrane equilibria to dyeing processes is combined with a recognition of salt linkages between the long-chain protein molecules of wool, increased precision can be given to the chemical theory of dyeing. The reaction between wool and acid would be written not as protein + acid = protein salt + water, but as, for example:

arginine glutamate + HCl = arginine chloride + glutamic acid,

except that the arginine and glutamic acid are bound into the long peptide chains through  $\alpha$ -amino and carboxyl groups. Recognition of the salt linkage has the merit of explaining why acid dyes can be adsorbed by wool from neutral solution, a fact which has often been advanced as argument against the strict chemical theory of dyeing. In neutral solution, the reaction between wool and acid dyes is a simple double decomposition, which may be written as:

arginine glutamate + Na $\overline{\text{Col}}$  = Arginine- $\overline{\text{Col}}$  + sodium glutamate.

Some years ago, I attempted a reconciliation of the several theories of dyeing in terms of Loeb's application of the Donnan theory to proteins, and it is interesting to find that recent studies of the action of acids on wool strengthen the view then advanced, especially as regards the solid solution hypothesis. It has been shown that acids have the ability to open the salt linkages in the molecule, thereby separating the protein chains from one another. The micelle structure is dispersed, more completely in the case of weak acids, and the whole structure is uniformly accessible to the dyestuff. In other words, dye adsorbed by wool is in simple solid solution, except that it is retained by strict chemical combination with the basic groups of the side chains of the long-chain molecules.

In conclusion, I would add that Professor Elöd's paper contains data from which a complete titration curve of wool with hydrochloric acid may be derived, and in this respect he has anticipated the corresponding data in our paper on "The Constitution of the Keratin Molecule."

**Professor F. G. Donnan** (London) said: I have been deeply interested in the work on the dyeing of protein fibres which Professor Elöd and his pupil Silva have published. I wonder whether Professor Elöd could test his theory by using protein gels or films instead of natural fibres? As regards the discrepancies found by F. Böhme (working

<sup>&</sup>lt;sup>1</sup> J. Soc. Dyers and Colourists, 25, 172, 1925.

under the direction of Professor Elöd), I might mention that deviations of a similar type have been observed in the distribution ratios of chloride and bromide ions between the inner contents of red blood cells and the outer blood serum.<sup>2</sup>

Dr. J. R. Katz (Amsterdam) said: The experiments of Professor Elöd are, I think, very important not only for the theory of dyeing, but also for the theory of swelling in general. All the fibrous substances which are dyed are swelling substances. As dyes are ionising substances, what Professor Elöd has worked out for dyes is a special case of a more general phenomenon, the influence of ionising substances in swelling. We therefore find in Professor Elöd's investigations valuable contributions to our knowledge of swelling in aqueous solutions of ionising substances and of the rôle played in it by the absorption and adsorption of the ions.

Professor Elöd, in reply, said: I am of the same opinion on the reaction capacity of proteins at the isoelectric point as Dr. Speakman. Doubtless only a minimum of the reaction capacity exists there, but it is not wholly lacking. The formation of molecular combinations is quite possible. If this were not the case, no explanation could be given, for instance for the chromic tanning of skins by different chromium complexes, which goes on with some complexes chiefly at the iso-electric point. The taking up, too, of dyestuffs by no means ceases at the iso-electric point.

It is very probable that in other dyeing processes also, similar effects as those mentioned play a part. I am very grateful to Professor Donnan

for his proposals.

The swelling processes doubtlessly have a decisive influence on the dyeing processes. Also the weighting of silk is greatly influenced by these. I agree with Professor Katz in this matter. It is only remarkable that whereas in the weighting of silk the tensile strength of the fibre, in spite of high charging (about 40 per cent.) with tin salts (with which a marked increase of the volume is connected—swelling!) shows only little change (provided that secondary effects are eliminated). Skin fibre, on the other hand, if charged with 20 per cent. of  $\text{Cr}_2\text{O}_3$ , decreases enormously in tensile strength. (The tensile strength of the skin fibre is of the same value as that of silk.)

**Professor H. Mark** (Wien) said: When we consider the dyeing properties of fibres and seek a scientific explanation for the amount of dyestuff fixed on the surface of a fibre we must have regard to the fact that this amount depends on two quantities: on the size of the surface of the fibre and on the heat of adsorption of the dyestuff. The first gives a member nearly independent of the temperature, while the factor which includes the heat of formation of the compound fibre-dyestuff is highly dependent upon the temperature.

If we want to get a true picture of the situation in any distinct case we have to measure the influence of the temperature and to separate the two just mentioned factors from each other. This corresponds with the separation of surface and heat of adsorption which is usually carried out in the treatment of catalysts.

**Professor Elöd**, in reply, said: In the dyeing processes discussed in my paper, the fibres are always homogenously dyed throughout the entire cross-section. As shown by our experiments, it is true that the

<sup>&</sup>lt;sup>2</sup> Hastings and Van Dyke, J. Biol. Chem., 78, 35, 1928; Colloid Symposium Monograph, 6, 153, 1928.

adsorption of the dyestuffs by the fibre play a noticeable but only an unimportant part and that only in the first stage of the process. The entire process is to a great extent directed by the pure chemical partial

processes.

The influence of the temperature was naturally taken into consideration in our experiments and was of importance for the investigation of the various partial processes mentioned in my paper. But it was such as could be expected in chemical processes and thus not as Professor Mark seems to suppose.

# THE RAISING OF THE SOLUBILITY OF DYE-STUFFS BY NEUTRAL SALTS.

By Wolfgang Ostwald.

Received in German on 26th July, 1932, and translated by H. E. L. Freytag.

I. The best known action of neutral salts on dyestuffs, particularly on those of the substantive type, is the salting out effect. Probably every substantive dyestuff is precipitated by higher concentrations of salts; in the case of the more highly dispersed dyestuffs, owing to solubility depression, for example, according to the mass action law. In colloidal dyestuffs neutral salts have a typical coagulating action (e.g. Congorubin). The effect obeys the Schulze-Hardy rule, and is repressed by protective colloids, etc., corresponding completely to the behaviour of, say, a gold sol.1

In addition to these well-known phenomena, however, there are in the literature isolated references indicating other effects of neutral salts. Thus, salts are added to dyebaths for the purpose of "equalising". According to R. Haller and A. Novack 2 such additions of salts bring about a suitable medium or optimum adjustment of particle size. The results of these authors show furthermore that, not only do the neutral salts regulate the particle size, but they may even raise the solubility, for instance in the case of cotton red. Some dyestuffs precipitate on dialysis. The flakes do not redissolve in water, but are dissolved in dilute sodium chloride.

The author pointed out a few years ago the importance of these observations as well as the apparently quite general fact that, in the case of substantive dyestuffs, neutral salts have not only a solubility depressing and coagulating effect, but may also bring about an increase in the solubility and dispersion.3 Together with R. Tanaka 4 he showed by some fairly careful measurements that in a Congo blue sol, for instance, the colour change due to neutral salts does not depend on a change of the [H] but on the dispersing and/or dissolving 5 action of neutral salts. Analogous effects have since been found with sulphoncyanin by Wo.

<sup>&</sup>lt;sup>1</sup> Wo. Ostwald, Koll. Beih., 10, 179, 1919; 11, 74, 1919; 12, 92, 1920.

<sup>2</sup> R. Haller and A. Novack, Koll. Beih., 13, 86, 1920.

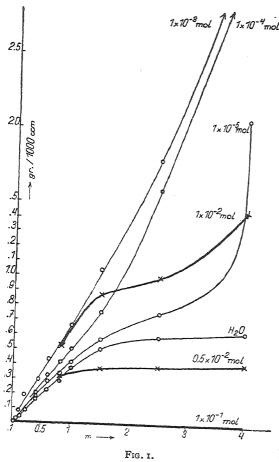
<sup>3</sup> Wo. Ostwald, Ber., 62, 1194, 1929.

<sup>4</sup> R. Tanaka, Koll. Z., 53, 200, 1930; 54, 156, 1931.

<sup>5</sup> By "dissolution" is here understood the change from a system dispersed micelled to one dispersed into melocules (a g, that occurring on the addition into micelles to one dispersed into molecules (e.g. that occurring on the addition of alcohol to a mastic hydrosol, of  $\mathrm{HNO_3}$  to a Ag-sol, and of  $\mathrm{NH_4OH}$  to a Ag-Brsol, etc.).

Ostwald and H. Rudolph 6 as well as with dianil blue by W. Schramek and E. Götte.7

It is characteristic for these neutral salt effects (as opposed to the usual effects) that increase in solubility and decrease in particle size occur, in the first place, at different (as a rule lower) concentrations than the salting out effects. It is, moreover, of importance that, in the case of colloidal systems, the two effects can occur at the same concentration but distinct from one another as to time. Thus the effect



of a certain addition of a neutral salt can be first to coagulate and only then to dissolve. The kinetics of both these processes is importance.8

2. We shall describe below a specially case, studied by the author together with Mr. R. Walter, of the solubility creasing effect of sodium sulphate the typical cotton dyestuff, benzo - purpurin 4B. Details of the purification, technique, as well as the figures, will be given elsewhere. In brief, it is a matter of solubility determinations at 25° with varying quantities solid phase present and different concentrations of sodium

sulphate. Figs. 1 and 2 represent the most important results graphically. In contrast to the solubility of molecularly dispersed substances, it has been shown by a comprehensive series of experiments 9 that the

Wo. Ostwald and H. Rudolph, Koll. Beih., 30, 416, 1930.
 W. Schramek and E. Götte, Koll. Beih., 34, 218, 1931.

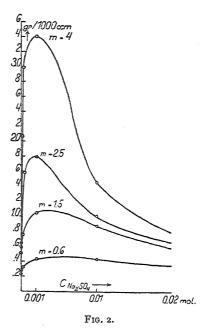
<sup>8</sup> A Ag-sol is thus usually first coagulated by HNO3 and only then dissolved; A Ag-sol is thus usually hist coagulated by throg and only then dissolved, the same holds for a Au-sol + KCN; cf. the quantitative studies of R. Auerbach, Koll. Z., 28, 124, 1921; and, for Congo blue, of R. Tanaka, loc. cit.

9 Wo. Ostwald, A. von Buzagh and collaborators, Koll. Z., 41, 43, 49, etc.;

maximum amount taken up in colloidal solution is *not* independent of the quantity of solute added or of solid phase present. It is quite general for colloidal dissolution that the amount passing into solution at first tends to increase as increasing quantities of solid phase are added. According to the type of dissolution occurring (peptisation by adsorption, peptisation by solution, solubility of a mixed substance, autopeptisation, etc.), we obtain curves which only increase or also curves showing a maximum, where the solubility falls again when still greater amounts of solid phase are used.

In Fig. 1 the amount of solute used or of solid phase present, m, (grams per 1000 c.c.) is taken as abscissa and the solubility (grams per 1000 c.c.) as ordinate. The individual curves ( $\rm H_2O$ , 1  $\times$  10  $^{-5}$  mol,

etc.) show the solubility with varying amounts of solid phase present and varying Na<sub>2</sub>SO<sub>4</sub> concentrations. In the region investigated rising curves are predominant; the solubility rises continually as the amount of solute used is increased. Only in the most concentrated salt solution (0.1 molar) is a decrease (small absolutely but relatively unmistakable) found quantitatively in the solubility as the amount of solute used is increased: 30-20—16—10—7—7—6—6—(× 10<sup>-4</sup> grams per 1000 c.c.). Between 0.05 and 0.1 molar Na<sub>2</sub>SO<sub>4</sub> a curve with a maximum could probably be obtained. Finally, the form of the curves indicates that we are presumably considering a case of autopeptisation; an "easily soluble" fraction (passing into solution first) of the polydisperse dyestuff promotes the solof another, "difficultly ution soluble," fraction.10



In addition to this effect of the solid phase present, however, the curves and tables show in the plainest manner the twofold action of the neutral salt, especially its marked power of increasing the solubility of the benzopurpurin. This effect is already noticeable with very small Na<sub>2</sub>SO<sub>4</sub>—concentrations. Thus a 0.00001 molar solution of Na<sub>2</sub>SO<sub>4</sub> shows (whatever quantity of solid phase may be present, but especially when this is large) a power of dissolving benzopurpurin quite considerably larger than that of pure water. When 4 grams of solid phase are present per litre three times as much dyestuff passes into solution in this extremely dilute salt solution as in water. At first the increase in solubility rises with the concentration of salt. Between 10<sup>-3</sup> and 10<sup>-2</sup> mols of Na<sub>2</sub>SO<sub>4</sub> per litre this effect has, however, reached its maximum. When the concentration is increased further, say to 10<sup>-2</sup> or still higher, the increase

<sup>&</sup>lt;sup>10</sup> For analogous conditions in the dissolution of acetyl cellulose, cf. Wo. Ostwald and H. Ortloff, Koll. Z., 58, 215, 1932.

in solubility is replaced by a decrease, and with a 0-1 molar Na, SO, solution we have the well-known phenomenon of almost complete salting

out by the neutral salt.

This twofold function of the neutral salt is shown more clearly and comprehensively in Fig. 2, in which the abscissæ represent salt concentrations (up to 0.02 molar) and the ordinates the solubilities as before. The four curves correspond to the presence of four different amounts of solid phase, which are therefore constant for each curve. A series of regular curves with maxima results. The smaller concentrations raise the solubility up to a maximum; with further increase of the concentration decrease in solubility and salting out occur.

- 3. The effect here described of neutral salts on the solubility of a colloidal dyestuff has a noticeable resemblance to the effect of neutral salts on the solubility of certain albuminous substances, especially of the globulins. In the first place, the solubility in neutral salts of the globulins also depends on the amount of solid phase present, as we know from the classic work of W. B. Hardy, W. Mellanby and S. P. L. Sörensen. 11 Further, however, the effects of the salt on the solubility are the opposite to one another according to the concentration. Quite analogous curves with maxima are obtained, and it is well-known that globulin is not soluble in pure water, but is soluble in dilute salt solutions, while it is precipitated again by high concentrations of salt.
- 4. The effect of suitable concentrations of neutral salts in raising the solubility is also of interest for the practical dyeing industry. The upshot is that the salt added to technical dyestuffs should by no means be regarded merely as an impurity or adulterant, but as an agent which can, in addition to regulating the taking up of dyestuff by the fibre, also raise the solubility of the dyestuff (at least in some cases), which is quite the opposite to the salting-out effect by higher concentrations which alone is usually regarded. With regard to this, a comparison consideration, the maximum solubility was found at a concentration of about 0.001 mol, i.e. of about 0.322 gr. Na<sub>2</sub>SO<sub>4</sub>, 10H<sub>2</sub>O per litre. When 4 gr. of dyestuff is added per litre, 3.41 gr. is dissolved, while pure water can only dissolve 0.63 gr. Expressed in mols, one millimol of Na<sub>2</sub>SO<sub>4</sub> can dissolve about 5 millimols of benzopurpurin (when 4 gr. per litre is added), while pure water barely takes up I millimol (M.W. = 682). In pure water, therefore, only about 16 per cent. of the added dyestuff would be dissolved and available for the fibres and in this salt solution, on the other hand, more than 82 per cent. The raising of the solubility by suitable additions of neutral salts is consequently also of importance practically.

Summary.

- 1. It is pointed out from the author's work and that of others that the action of neutral salts on substantive dyestuffs may not only be to bring about salting-out but, at suitable concentrations, may also exhibit the opposite effect of raising the solubility.
- 2. As a specially good case, that of benzopurpurin 4B and sodium sulphate is described. Here the solubility not only markedly depends upon the quantity of solid phase present (amount of solute added) but also increases rapidly at low salt concentrations, reaches its maximum with about o ooi molar Na<sub>2</sub>SO<sub>4</sub> and only then begins to fall off owing to

<sup>11</sup> Literature and summary: Coll. Z., 49, 188, 1929 or M. Spiegel-Adolf, Die Globuline (Handb. der Kolloidwissenschaft, Leipzig, 1930, p. 277, Fig. 47).

salting out. The solubility in dilute sodium sulphate is more than five times that in pure water. A marked increase in solubility is already caused by a concentration of o oooor mols Na<sub>2</sub>SO<sub>4</sub> per litre.

3. Attention is drawn to the analogy between the action of neutral salts on substantive dyestuffs and on proteins of the globulin type.

4. The technical importance of this increase in solubility due to small concentrations of salt is also briefly mentioned.

#### GENERAL DISCUSSION.

Mr. J. Boulton (Braintree) said: In the absence of the author one hesitates to discuss this paper at any length, since the principal value of any discussion would lie in the viewpoint of Professor Ostwald and in his answers to the questions one might wish to raise.

In describing work, particularly quantitative work on dyes or dyeing, the all-important question is that of whether or not one has obtained a pure dyestuff in the first place; whether or not experimental results do refer to a chemical individual. Professor Ostwald does not include in his paper the method employed by him for the obtaining of pure benzopurpurine. With regard to the effect that forms the subject of his paper he refers, however, to a paper by Schramek and Götte. two workers who made analogous observations with another dyestuff, dianil blue, and in which the authors state that they obtained minimum dyeparticle size in the presence of an inorganic salt. In this latter case, examination of technique and results indicates that a pure dyestuff was not employed in making their observations. The method of precipitating and purifying the free dye-acid followed by attempted quantitative neutralisation to produce the sodium salt which is the actual dye apparently results in a mixture of the free acid and the dye itself, the former existing as occluded particles in the neutralised dye.

Protracted experiments on the absorption of direct dyes by cellulose has, since they are necessary to a quantitative study, lead the present speaker and colleagues to cast round for methods of both purifying and estimating the purity of certain dyestuffs. The only satisfactory method to appear, so far, in the literature, for the purification of benzopurpurine 4B. is that due to Robinson and Mills.<sup>2</sup> It is worthy of note that the figure given by these workers for the solubility of pure benzopurpurine 4B. in water is much higher than that inferred from Professor Ostwald's

Solutions of benzopurpurine have been found to be very sensitive to electrolyte additions: polyvalent ions introduced by dissolution of the walls of glass vessels have been found to precipitate some of the pure dye from solutions of certain concentrations.

The effect described by Professor Ostwald might be explained, assuming the presence of some free dye-acid in his solid dye; it is quite feasible that base exchange in the presence of an inorganic salt should cause the water-insoluble dye acid to dissolve and thus produce a higher figure for the solubility of the "dye" in dilute salt solution than that obtained

A warning has been given to this meeting in connection with cellulose. Mr. Neale has remarked, in this connection, that one must purify carefully and characterise adequately one's material. The same may be

<sup>&</sup>lt;sup>1</sup> Koll. Beih., **34,** 1931.

said of dyestuffs. Apart from technical observations, often of value, a great part of the literature dealing with dye absorption is useless as a result of workers employing impure dyes. Those workers engaged in this field of research who appreciate the difficulties experienced in purifying and estimating dyestuffs, particularly those of the direct dyeing class, must also appreciate those physico-chemical investigations, on the lines of the paper under discussion which help to throw light on the general properties of the really little understood class of colouring matters . . . direct dyestuffs.

**Dr. Commar Robinson** (London) said: I cannot help being interested in Professor Ostwald's paper as I have carried out a considerable amount of work on benzopurpurine during the last three years.

Last year Mr. H. A. T. Mills and I published a paper in which we described the properties of pure benzopurpurine. We considered, I think rightly, that the samples we prepared were the purest so far obtained. An accurate determination of the solubility was difficult on account of the difficulty of separating the solid dye from the saturated solution. We did, however, find that the solubility was approximately 8 grms. per litre (equilibrium being reached from both sides in these determinations). No dependence of the solubility on the quantity of "Bodenkörper" was detected, but the results were not sufficiently accurate to detect a small variation.

Now Professor Ostwald gives about 1/13 of this as the solubility of pure benzopurpurine (0.6 grms. per litre). He claims that a large increase in solubility is brought about by as little as .00001 grms. per litre of Na<sub>2</sub>SO<sub>4</sub>. This might suggest that our dye contained an electrolyte impurity of this order, such a small amount of impurity being certainly quite possible, and that this impurity had increased the solubility.

But if we look at Fig. I we find that even with large Na<sub>2</sub>SO<sub>4</sub> concentrations the highest solubility he obtains is not 1/4 of that which we obtained. So that the two sets of results cannot be reconciled.

We have done a large amount of our work with 0.5 per cent. solutions and never obtained any indication that these were supersaturated. They are optically empty and remain unchanged indefinitely if  $\mathrm{CO}_2$  is excluded. The conductivity, viscosity and transport number (results shortly to be published) are reproducible to one part in several hundred, while the osmotic pressure and diffusion coefficient were shown to be as reproducible as the experimental method allowed. This reproducibility of the properties of pure dye solutions is not always recognised by workers in this field.

Considering this reproducibility and constancy of the properties of the pure solutions, it seems surprising that Professor Ostwald finds the solubility varies with the amount of "Bodenkörper." One naturally wonders if this is not itself evidence of the impurity of his dyestuff, but perhaps Professor Ostwald will be able to satisfy us on that point when he publishes the experimental details.

Assuming that Professor Ostwald's results represent the solubility of pure dye in the presence of  $\rm Na_2SO_4$  it is difficult to understand what the mechanism of the increase in solubility can be. If I  $\times$  10<sup>-5</sup> grms. per litre of  $\rm Na_2SO_4$  increase the solubility from 0.6 to 2.0 grms. per litre, this means that one molecule of  $\rm Na_2SO_4$  greatly increases the solubility of several hundred molecules of dye. What does the small amount of  $\rm Na_2SO_4$  do?

<sup>&</sup>lt;sup>3</sup> Robinson and Mills, Proc. Roy. Soc., 131A, 576, 1931.

It cannot appreciably alter the properties of the solvent, so presumably it must be an effect at the surface of the micelle. If we had in place of the dye a non-electrolyte, we might suppose it altered the charge. The micelle here, however, is made up of ions, and it seems very difficult to see how the one molecule of Na<sub>2</sub>SO<sub>4</sub> could greatly affect the electrical condition of the micelles built up from the ions of several hundred dye molecules which already contain a large charge.

Mr. S. M. Neale (Manchester) said: The remarks of Mr. Boulton and Dr. Robinson on the question of the solubility of Benzopurpurine 4B are in complete accord with experience in my laboratory, where exact measurements of the absorption of dyestuffs by cellulose are in progress. In our opinion chemical methods of assessing the purity of a dyestuff, though giving an ostensibly absolute figure, really give a maximum which is far too high, since they include isomerides and homologues of low colouring power. More specific—though purely relative—information is obtained by the colorimetric comparison of various "pure" samples and by accurate measurements of absorption on cellulose.

**Dr. Büchner** (Amsterdam) said, with regard to Dr. Robinson's remarks, that it was important to be sure that the benzopurpurin was crystalline. The solubility could only be defined with relation to a definite phase, effects of grain size being excluded. This was a matter always to be borne in mind when the solubility of colloidal substances was discussed.

Professor Ostwald, in reply, wrote: With regard to the remarks of Mr. Boulton I had thought it was well known and recognised that the application of the ordinary conception of "chemical purity" to colloid systems is quite impossible. "Purity" in colloid chemistry does not signify, as in ordinary chemistry, "chemical individuality." In colloid chemistry "purity" signifies only the greatest possible "simplification" of the chemical composition (so long as thereby the colloid properties are not destroyed) and secondly the most quantitative possible "definition of the composition." No one has ever seen a chemically pure gold sol; it always consists of gold and gold salts in changing proportions. There is no doubt that Pauli has shown that by electrodialysis albumin can be obtained practically ash-free. Nevertheless, Sørensen in his classical work did not use this "chemically pure" salt-free albumin but the so-called "egg sulphate," which is a mixture of albumin, ammonium sulphate and varying, but known, quantities of free NH<sub>4</sub>OH and H<sub>2</sub>SO<sub>4</sub>. Why was this? Because, shocking though it may appear to the pure chemist, in the case of this colloid it is not the chemically pure individuum which crystallises, but, on the contrary, only the complex mixture. Sørensen saw, however, in the crystallisability a sharper definitive criterion of his starting material than in the freedom from ash.

In collaboration with my colleagues I have for more than twenty years, on many occasions and by very different methods, "purified," in this sense, very different colloid dyestuffs; for instance, by prolonged cold and hot dialysis in water or in electrolytes, by extraction with cold or boiling alcohol, acetone, etc., by purification with several organic solvents in succession, by adsorption on charcoal from water and elutriation with alcohol, by ultra-filtration of various kinds, by electrodialysis, by chemical synthesis, etc., I have "purified" congorubin

by some ten methods in parallel experiments.<sup>4</sup> I have been fully seised of the importance of this point.

The curves I have given indicate only a representative selection from a systematic series of experiments in which the solubility of the following derivatives of benzopurpurine in neutral salts was investigated: pure dye-acids, those containing one Na atom (or acid salts), those containing two Na atoms (or neutral salts), and lastly those containing an excess of NaOH. The importance of investigating the graded reactions between dye acids and neutral salts arises from the following observation, viz., that with exactly equivalent quantities of alkali dyeacids are not fully soluble. I do not believe that the reason of this is "occlusion" of the dye-acid; rather I believe that an excess of alkali is necessary for colloidal solution or peptisation. On the other hand, an excess of mineral acid is necessary for the complete precipitation of the dye-acid from the salt as has been shown by A. Hantsch in the case of congo-red.<sup>5</sup> The addition of exactly equivalent quantities of HCl turns congo-red only dirty red; it is not until there is an excess that it turns blue. This excess of acid is in my opinion used up in the colloid precipitation of the highly dispersed acid sols. This means that the pure stoichiometric chemical definition does not suffice to define a neutral benzopurpin preparation. Quite apart from hydrolysis (which is generally found to a small degree), the presence of dye-acid in neutral solutions with a stoichiometric sodium content is possible from both the above points of view.

We have already with R. Tanaka (loc. cit.) published our results upon the solubility of dye-acids (congo-red) alone in neutral salts. In fact these observations formed the starting-point also for the above-mentioned investigations, and Mr. Boulton's idea as to the rôle these dye-acids might play in solution is not indeed new to us. The example given lies quite in the mean of this series of experiments. The preparations used (chlorine and sulphate free) contained exactly 3·17 per cent. Na, which would correspond to a half-neutral or acid salt. If one does not acknowledge the existence of such an acid salt, the experiment in question would refer to a quantitatively defined mixture of 50 per cent. dye-acid and 50 per cent. dye salt.

The preparation used for the curves shown is, moreover, not to be compared with the normal dibasic salt such as Dr. Robinson has used, and I regret that I made no reference before to this important point.

Complete data, which *inter alia* show that quite analogous solubility curves are given in neutral salts with strictly neutral colour salts containing two Na-atoms (e.g., Turkey red), just as with those abovementioned, will be published in the *Kolloid Zeitschrift*.

It may be that I do not fully understand the theory proposed by Mr. Boulton for the solution of dye-acids in neutral salts by "base exchange." If he means a reaction according to the equation:

Dye acid + 
$$Na_2SO_4 \leq sodium dye salt + H_2SO_4$$
.

I would say that I do not believe that the extraordinarily large increase in the solubility which we have observed can be explained in this way. According to our understanding, the neutral salt effect on dye-acids is a peptisation phenomenon, brought about by the intervention of additive compounds, in the sense of Pfeiffer's compounds of aminoacids and neutral salts.

Dr. Robinson asks how a single molecule of Na<sub>2</sub>SO<sub>4</sub> can have an effect upon 100 molecules of dyestuff. The answer is that in this case a salt molecule does not at all affect 100 single dyestuff molecules but, on the contrary (to take the same order of figures), 100 salt molecules act on a single dyestuff particle, for example, of microscopical dimensions, or perhaps on a microscopic aggregate of micelles. We can even imagine that a crystal lattice (e.g., a crystal needle), holding electrolyte in an electrolyte medium which surrounds its surface and is different to that of the crystal, has its equilibrium disturbed and is split up into fragments of colloidal dimensions; compare the experiments of P. Rehbinder 6 on the destruction of the surface hardness of crystals by adsorbed polar molecules. The correlation of single molecules of the dyestuff and single molecules of the neutral salt appears to me impossible on the basis of a peptisation, that is to say a colloidal, often irreversible, solution, as distinct from the reversible equilibrium of a molecular solution process postulated by Dr. Robinson.

<sup>6</sup> Z. Physik, 72, 191, 1932.

## SOME DIFFICULTIES IN COTTON YARN MERCER-ISATION.

By Dr. Paul Krais, Dresden.

(Textile Industries' Research Institute.)

Received 25th July, 1932.

It has been known for twenty-four years that mercerised cotton behaves differently in the dye-bath according as to whether it has been dried or not between the mercerising and the dyeing process. E. Knecht was the first to announce this fact in 1908. He stated that cotton yarn, mercerised under tension, takes up the following amounts of Benzopurpurine 4B:

#### TABLE I.

Not dried after mercerisation	n.	3.24 per	cent.,	calculated	in part	s: 100·0
Dried in the open air .		3.03	,,	,,	,,	93.8
Dried at 110° C	•	2.21	,,	,,	,,	77.5

No difference was found in the case of ordinary cotton, whether it was dried at 110° C., or not, before dyeing. E. Knecht further observed that the alteration which mercerised cotton undergoes on drying is a complete one, not being reversed even by prolonged treatment with running water or dilute acids or alkalis. Repetition of the mercerising process is the only means of curing such faults as are caused by irregular drying between mercerisation and dyeing.

This knowledge has been well kept in mind by all mercerisers and textile chemists, so that serious faults have occurred but rarely. A very curious change in fashion (or rather two changes) during the last two or three years has brought up this difficulty afresh. The first was the fashion of ladies' short skirts, which gave the stockings an importance

hitherto unknown. All went well, however, so long as the fashionable stocking shades were very light salmon, orange, drab, silver, even skyblue and seagreen. In order to dye these the stockings had to be well boiled out and bleached before dyeing. But the second change of fashion brought about a demand, instead of for bright shades, for dull browns and dark greys exclusively, and this appears likely to remain in demand for some time to come. The boiling out and bleaching is now superfluous, which means, of course, much saving in labour and steam. But on the other hand every minute difference in the mercerised cotton yarn shows itself now by unevenness in dyeing, the faults taking varied forms, such as ringlets (which are not fashionable), lighter or darker bars and spots, etc.

This problem had now to be investigated most carefully again, and we have found no less than thirty possibilities, which may lead to uneven

dyeing in mercerised cotton hosiery.\*

Many of these points are of interest to the textile chemist, others concern more the engineer. In order not to be too lengthy, I will refer only to three of them: (1) difference in drying, (2) traces of mineral acid, (3) influence of light and air.

The faults caused by different degrees of drying have been mentioned above, but I might also give some new data, which confirm and expand E. Knecht's statement. Egyptian cotton yarn, mercerised without tension in 54° Tw. caustic soda lye at ordinary temperature, rinsed, soured, and rinsed again, gave the following colour measurements according to Wilhelm Ostwald's method, the final dyeings being made all in one bath with Diamine Black BH, after thoroughly wetting out the hanks in a hot solution of Nekal BX:

TABLE II.†

	Colour Shade.	Black. Per Cent.	White. Per Cent.
1. Dyed in the wet condition, without drying			
beforehand	14.0	91.9	2.4
before dyeing	14.4	88·o	4.4
open air overnight, then dyed	14.6	85·o	5.9
4. Dried in the open air, then at 110° C., then hung out and dyed	14.65	85.0	5.8

The differences in colour are not very remarkable, and it is evident that there is no marked difference at all between Nos. 3 and 4. But the difference in White, which is in direct relation to the depth of the shades, No. 1 being the darkest, No. 2 medium and Nos. 3 and 4 the lightest, is quite evident.

We must assume, so it seems, that the highly swelled condition of the cotton fibre after mercerising and washing is most favourable for the taking up of direct dyestuffs, and that this condition is reduced

<sup>\*</sup> For details I refer to our publication in *Textile Forschung*, Dresden, No. 1, 3, 1931.

<sup>†</sup> For these measurements, as well as those in Table III., I desire to record my grateful thanks to Prof. Dr. Klughardt of the Colour Investigation Department of our Institute.

permanently and in degrees by drying at different temperatures. (An intermediate state is reached if we dry at 50° C.) There is, so to say, a de-swelling formation (*Entquellungssustand*), which is dependent on the drying temperature, independent of consequent wetting out, independent also of whether the cotton has been mercerised under tension

(Knecht) or without (Krais).

The second point is, that minimal traces of mineral acids can have a very marked influence, even after they are completely removed. Mercerised cotton is quite absurdly sensitive in this respect. When a hank of mercerised cotton is impregnated at ordinary temperature with N/500 hydrochloric acid and squeezed out, it contains about 0.013 per cent. HCl. If this hank is dried at 100° C., washed thoroughly in alkaline water and dyed (Diamine Black BH) in the same bath with a nontreated hank of the same mercerised yarn, there is a difference in shade, which is sufficiently strong to make goods unsaleable. With N/1000 acid no difference is to be seen.

The measurements are as follows:--

TABLE III.

				 	Colour Shade.	Black. Per Cent.	White. Per Cent.
<ol> <li>Not treated</li> <li>N/500 HCl</li> <li>N/100 ,, .</li> </ol>	:	:	:	•	14·85 14·95 15·0	87·8 86·9 86·0	5·2 5·7 6·2

The result is that the merceriser must be very careful to leave no trace of acid in the yarn that goes into the drying oven. The question is whether these different dyeing properties are caused by superficial formation of hydrocellulose, or by a change of the isoelectric point, or by some other change.

The third difficulty, change by light and air is more difficult still. Of course we can understand that mercerised cotton yarn, when stored in bundles, the ends of which are exposed to light, will change by the fading of the natural brownish dyestuff, which is characteristic of Egyptian cotton. This will, under modern conditions (no boil, no bleach, brown shades), lead to uneven dyeings. But there seem to be some subtler influences also, of which we have no knowledge yet.

From all this it is apparent that mercerised cotton in the raw state is, in spite of its otherwise excellent qualities (increased lustre, tensile strength, affinity for dyestuffs, etc.), a very sensitive material, the study of which is most interesting, difficult and incomplete. We must not forget that during mercerisation a new cellulose compound, namely, sodium cellulose, is formed and decomposed again, and that great swellings and contractions take place.

# THE EMULSIFICATION OF MIXED LIQUIDS OF HIGH MOLECULAR WEIGHT.

By J. B. Speakman, D.Sc., and N. H. Chamberlain, Ph.D.

Received 25th August, 1932.

In order to facilitate manipulation of the fibres, oil is applied to wool prior to carding and combing. Its subsequent removal, by means of soap and soda solution, presents an interesting problem in the theory of emulsification and detergent action. As regards the woollen trade, the oils employed consist mainly or entirely of oleic acid, and their removal is brought about simply by saponification with soda. Chief interest is therefore associated with the worsted trade, where oils containing not more than 5 per cent. of free fatty acids are customary. The amount normally used in combing is 3 per cent. by weight, and if this is assumed to be uniformly distributed over wool having an average fibre diameter of 20  $\mu$  (64's quality), the thickness of the oil film is of the order of 0.2  $\mu$ . It is here that theoretical interest is aroused, because Hardy, using plane surfaces separated by fluid media, obtained evidence of molecular orientation in films up to 5 or 7  $\mu$  thickness. In the case of oil films less than I  $\mu$  thick a highly organised structure must therefore develop by the processes of molecular orientation and diachysis; adhesion between oil and wool will become significant and increase with the chain length and polar character of the oil molecules; and adhesion of this type, together with cohesion within the film, must oppose removal of oil by emulsifica-Similarly, it is now recognised that liquids in bulk are not free from structure, and incipient crystallisation (the cybotactic condition), increasing with the chain length and polar character of the molecules. has been detected by Stewart 2 and others, using X-ray technique. Hitherto it seems to have been assumed that the ease of emulsification of oils by means of soap solution is governed simply by the magnitude of the interfacial tension and the formation of a stable adsorbed film at the interface, but it now seems probable that, whether the oil is distributed as a thin film on a solid surface or is present in bulk, emulsification will be opposed by molecular adhesion in one or other of its various manifestations. Although the following experiments, which were designed to discover the importance of such adhesion phenomena, are essentially industrial in their purpose and method, they have an undoubted theoretical interest which may justify the general title chosen for the paper. In addition, they have a specific interest for the worsted section of the wool textile trade. As has already been indicated, the oil applied in combing is distributed as a thin film which exposes an enormous surface to the atmosphere. The risk of oxidation is high, and oxidised oil resists emulsification with soap to such an extent that none but non-drying oils can be used as wool lubricants. Of those available, olive oil has found general favour and, in this country at least, is employed to the exclusion of other types. At first sight it would be ex-

<sup>&</sup>lt;sup>1</sup> Hardy, Phil. Trans., 230A, 1, 1931.

<sup>&</sup>lt;sup>2</sup> Stewart, Reviews of Modern Physics, 2, 116, 1930.



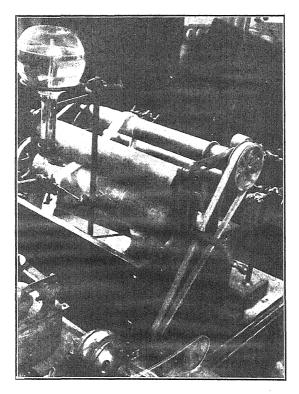


Fig. 1. [To face page 359.

pected that mineral oil, being completely free from oxidation risk, and less expensive than olive oil, would succeed in displacing the latter. Actually, mineral oil is never used as a wool lubricant because it is impossible to remove it by emulsification with soap and soda solution. The reason for this peculiarity has never been established, and an endeavour has been made in what follows to combine two purposes: to discover the part played by adhesion phenomena in emulsification, and to establish the reason for the difficulty experienced in removing mineral oil from wool.

#### Experimental.

#### Procedure.

As regards textile technology, the chief interest of these experiments lies in their relation to the piece-scouring operation, and the method of experiment is essentially such an operation in miniature. Strips of a white worsted fabric, each 21 inches wide and 56 inches long, weighing approximately 25 grams, were used. Each of these was conditioned for twenty-four hours in a room maintained at 72° F. and 65 per cent. relative humidity, and then weighed precisely before use. The amount of oil to be applied was weighed out in a 250 c.c. beaker, and sufficient ether added to ensure that complete wetting-out occurred when the rolled-up strip of cloth was introduced. A small amount of ether solution remained in excess, and the beaker was tilted to one side and rotated in this position so that the cloth turned continuously in the solution as the ether evaporated. When no solution remained free, the strip of cloth was removed rapidly, extended to its full length while held at each end, and then swung to and fro in the air until all the ether had evaporated. In this way, the weighed strip of cloth was impregnated with a known weight of oil and uniform distribution ensured. The cloth was then introduced into the scouring machine, as shown in Fig. 1, the two ends being sewn together with cotton to form a continuous rope. To prevent the cloth running in well-defined folds during an experiment, nine turns of twist were inserted before the ends were sewn together.

At this stage the machine was started and the speed adjusted to an arbitrary standard by means of the sliding resistance; 100 c.c. of a 0.4 per cent. potassium oleate and 2 per cent. soda solution were then introduced into the porcelain dish at the base of the machine. The solution absorbed by the cloth on its way up to the squeeze rollers was there removed, together with any emulsified oil, and returned to the dish by way of the inclined lead trough under the rollers. After fifteen minutes the lead trough was inclined in the opposite direction, so that the solution squeezed out of the fabric was transferred to a second dish out of contact with the cloth. When all possible liquid had been removed, the lead trough was returned to its former position, and 100 c.c. of a 0.4 per cent. potassium oleate solution added as before to the porcelain dish. In all cases very little, if any, removal of oil occurred during the first of the two scouring operations. This is due to the fact that wool has an enormous affinity for alkali, which necessitates the presence of soda to avoid excessive formation of acid soap, and soda has a saltingout action on the soap which prevents lathering. The use of soap and soda in conjunction was commenced in preliminary experiments with olive oil where an endeavour was made to ensure complete removal of oil in one scouring operation. This was unsuccessful, and it was recognised that the most successful and economical practice is to use a 2 per

cent. solution of soda in the first bath, followed by 0.4 per cent. soap solution in the second. The soda satisfies the affinity of wool for alkali before the application of soap, so that alkali adsorption from the soap solution does not occur, and the amount of soda left in the fabric after the first scouring process is insufficient to cause salting out. Comparable experiments with various oils showed that the use of soap in conjunction with soda in the first bath serves no useful purpose, the amount of oil retained by the cloth being independent of whether or not soap is present. Nevertheless, since certain experiments had been carried out using soap and soda together, the use of soap in the first bath was retained to ensure complete comparability of all results.

After fifteen minutes' scouring in the second (soap) solution, the lead trough was again tilted to drain off the emulsion. Warm distilled water was then run on to the fabric at a standard rate from an inverted wash bottle, the water being applied to the cloth near the point at which it entered the squeeze rollers. The process of washing-off occupied thirty minutes, and was carried out gradually at first to avoid "cracking" the emulsion remaining in the piece. Finally, the machine was stopped and the fabric removed, centrifuged and allowed to dry overnight. The amount of oil it retained after scouring was then estimated by ether extraction in a Soxhlet apparatus. Despite the crudity of the scouring machine, the above procedure gave precise and reproducible results, as will be seen from what follows.

#### Discussion of Results.

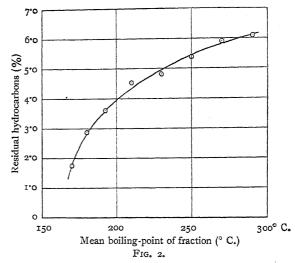
The first set of experiments to be carried out was intended to discover the part played by adhesion in opposing the emulsification of oil in scouring processes. A mineral oil freed from unsaturated compounds,  $d 25^{\circ}/4^{\circ} = 0.8672$ , was subjected to repeated fractional distillation to obtain a series of fractions covering a wide range of temperature. Strips of fabric were oiled with 10 per cent. by weight of each fraction, scoured as described above, and the residual oil estimated. In all cases the extracted oil contained a small amount of free oleic acid which was estimated by titration with alkali and subtracted from the total residual oil. The low-boiling fractions were not completely involatile on the water bath used to remove last traces of ether from the oil after Soxhlet extraction. To avoid any error due to this cause, the oil was heated for four successive periods of fifteen minutes and weighed at the end of each interval. The rate of loss of paraffin by evaporation was thus obtained and a correction applied for what had been lost during the first fifteen minutes' heating. The results are summarised in Table I:-

TABLE I.

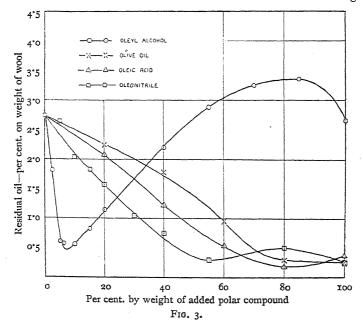
Boiling Range of Fraction °C. (Pressure = 10 mm. Hg.)	Residual Hydrocarbons. (Per cent. on Weight of Wool.)
165-175	1.80
175-185	2.90
185-200	3.59
200-220	4.54
220-240	4.82
240-260	5.37
260-280	5.90
280-300	6.10

From the graph, Fig. 2, it is evident that the difficulty of removing mineral oil from wool increases with the boiling-point of the fraction,

i.e. with the length of the molecule, to a remarkable degree. This, and the form of the curve, suggest that adhesion phenomena play a large part in determining the difficulty of scouring. The magnitude of the difficulty is emphasised by the fact that the fraction boiling 280°at 300° C. is retained to the extent of 61 cent. scouring. Although is thus



seen to be a factor of some importance in scouring processes, the failure to realise complete removal of the fraction boiling at 165°-175° C. is sufficient to show that this is not the sole cause of difficult scouring.



In the preceding experiment, surface tension considerations could be neglected in comparing the various fractions, because the oil-water interfacial tension is almost completely independent of the molecular weight of the paraffin. Owing to the non-polar character of mineral oil. however, interfacial tension is high and, quite apart from adhesion phenomena, emulsification must be difficult on this account alone. The importance of both factors is strikingly illustrated by experiments with mixtures of mineral oil and oleyl alcohol. The addition of oleyl alcohol to mineral oil reduces the oil-water interfacial tension, and on this account scouring should be facilitated. On the other hand, the marked polar character of oleyl alcohol will cause increased adhesion between oil and wool, and for this reason scouring should be more difficult. Which of the two factors will predominate can hardly be predicted, and experiments were carried out in which strips of fabric were oiled with 5 per cent. by weight of mixtures of mineral oil and oleyl alcohol in various proportions. The mineral oil used was that taken for fractionation; the oleyl alcohol was free from acid, and had an iodine value of 82.6. The amounts of oil retained by the several cloths after scouring were estimated in the usual way. Using the drop pipette, surface tension measurements were also made with the various mixtures at 25° C. against water, and against 0.1 per cent. potassium oleate solution, the values being reduced from drop numbers to absolute terms by the aid of Harkins and Brown's 3 data. The results obtained are summarised in Table II, illustrated by Figs. 3 and 4:-

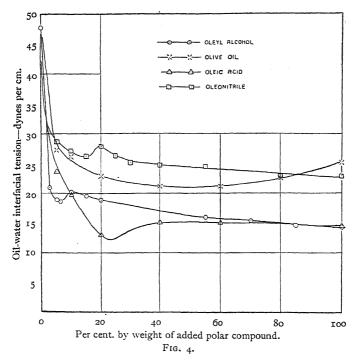
TABLE II.

Percentage by Weight	Oil-water Interfacial	Oil-soap Interfacial	Residual Oil.
of Oleyl Alcohol	Tension.	Tension.	(Per cent. on Weight
in Mixture.	(Dynes/cm.)	(Dynes/cm.)	of Wool.)
0·0	47·89	10·75	2·74
2·5	20·90	5·58	1·81
5·0	19·09	5·28	0·61
6·0	18·87	5·22	0·58
10·0	20·21	5·17	0·57
15·0	19·57	5·31	0·83
20·0	19·10	5·38	1·14
40·0 55·0 70·0 85·0 100·0	16·10 15·47 14·68 14·40	5·24 ————————————————————————————————————	2·20 2·88 3·25 3·36 2·66

Since the first small addition of oleyl alcohol to mineral oil causes a marked improvement in scouring, accompanied by a sharp fall in interfacial tension, it is evident that the high surface tension of mineral oil is the chief factor opposing emulsification. Perhaps the most interesting feature of the results is the fact that any increase in the content of oleyl alcohol beyond 7 per cent. increases the difficulty of scouring, despite the fact that the oil-water and oil-soap interfacial tensions continue, in general, to fall. Indeed, mixtures containing more than 55 per cent. of oleyl alcohol are more difficult to remove from wool than mineral oil. Such a result must be referred to increased adhesion between oil and wool, brought about by the polar character of oleyl alcohol. Since the right-hand arm of the scouring curve (Fig. 3) passes through the origin on extrapolation, adhesion must at first increase in strict proportion to the amount of oleyl alcohol present. It will, however, be noted that oleyl

<sup>3</sup> Harkins and Brown, J. Amer. Chem. Soc., 41 (1), 499, 1919.

alcohol itself is more easily removed from wool than the mixture containing 85 per cent. of this compound. Such a result is not in conflict with the present hypothesis, because it was observed that the fabric oiled with pure oleyl alcohol showed a curious appearance while still wet after scouring. It appeared to be covered with a soft paste, which had all the characteristics of an inverted emulsion. The formation of a water-in-oil emulsion must assist the removal of oil in the scouring machine, owing to the pressure applied at the squeeze rollers, and there is thus nothing unusual in the fact that oleyl alcohol is more easily scoured than the mixture containing only 85 per cent. of this compound. Apparently, in the case of thin films of oleyl alcohol on wool, adhesion becomes sufficiently pronounced for the alcohol to resist dispersion, and



it becomes the continuous phase in a water-in-oil emulsion. On the basis of this hypothesis, it is possible to offer an explanation of the curious observation made by Seifriz 4 during the course of his studies of emulsions. Using casein as emulsifier, he found that paraffins ranging in density from 0.664 to 0.828 gave emulsions of the oil-in-water type; those of density 0.857 to 0.895 gave emulsions of the water-in-oil type; while paraffins intermediate in density gave emulsions which separated immediately. No adequate explanation of the results appears to have been offered, but since the tendency for the oil to develop structure must increase with the length of the hydrocarbon chain, it seems probable that paraffins of low density give oil-in-water emulsions because little structure is present to resist dispersion; whereas paraffins of high

<sup>&</sup>lt;sup>4</sup> Seifriz, J. Physic. Chem., 29, 587, 1925.

density possess sufficient structure to oppose dispersion and water becomes the disperse phase. In other words, the type of emulsion formed in any particular instance depends, among other things, on the cybotactic state of the liquids concerned. It need hardly be said that oleyl alcohol in bulk is difficult to emulsify with soap solution, presumably because of a well-developed structure, whereas the mixture with mineral oil containing 6 per cent. of oleyl alcohol, and having a greater surface tension, forms an extremely stable emulsion under similar conditions. The formation

TABLE III.

Percentage by Weight of Added Polar Compound.	Oil-water Interfacial Tension. (Dynes/cm.)	Residual Oil. (Per Cent. on Weight of Wool.)
Olive Oil (containing o	o-89 per cent. of free fa	atty acid, calculated as
0	47.89	ſ 2·74
5	27.27	
10	26.23	
20	22.98	2.23
40	21.21	1.78
60	21.21	0.95
8o	22.66	0.31
100	25.26	0.27
Oleic Acid.		
0	47.89	2.74
5	23.65	- / -
10	19.66	
20	13.06	2.07
40	15.03	1.22
6o	15.01	0.56
8o	_	0.18
Oleonitrile. B.Pt. 2	14.60	o·38
Oleonitrile. B.Pt. 2	10°-215° C. under 15 n 47.89	nm. mercury pressure.
Oleonitrile. B.Pt. 2	10°-215° C. under 15 n 47.89 28.71	nm. mercury pressure.
Oleonitrile. B.Pt. 2	10°-215° C. under 15 n 47.89 28.71 27.02	nm. mercury pressure.  2.74 2.66 2.06
Oleonitrile. B.Pt. 2	10°-215° C. under 15 n 47.89 28.71 27.02 26.45	nm. mercury pressure.  2.74 2.66 2.06 1.82
Oleonitrile. B.Pt. 2.  0 5 10 15 20	10°-215° C. under 15 n 47.89 28.71 27.02 26.45 27.99	nm. mercury pressure.
Oleonitrile. B.Pt. 2	10°-215° C. under 15 n 47.89 28.71 27.02 26.45	nm. mercury pressure.  2.74 2.66 2.06 1.82
Oleonitrile. B.Pt. 2.  0 5 10 15 20 25	10°-215° C. under 15 n 47.89 28.71 27.02 26.45 27.99 26.64 25.25	2.74 2.66 2.06 1.82 1.57
Oleonitrile. B.Pt. 2.  0 5 10 15 20 25 30 40 55	47.89 28.71 27.02 26.45 27.99 26.64	2.74 2.66 2.06 1.82 1.57
Oleonitrile. B.Pt. 2:	10°-215° C. under 15 n 47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87	2.74 2.66 2.06 1.82 1.57 1.06
Oleonitrile. B.Pt. 2.  0 5 10 15 20 25 30 40 55	10°-215° C. under 15 n 47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87 24.67	nm. mercury pressure.  2.74 2.66 2.06 1.82 1.57 1.06 0.75 0.30
Oleonitrile. B.Pt. 2.  0 5 10 15 20 25 30 40 55 80 100  Methyl Oleate. B. 3	10°-215° C. under 15 n 47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87 24.67 23.03	nm. mercury pressure.  2.74 2.66 2.06 1.82 1.57 1.06 0.75 0.30 0.51 0.25
Oleonitrile. B.Pt. 2.  0 5 10 15 20 25 30 40 555 80 100  Methyl Oleate. B. 1	10°-215° C. under 15 n 47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87 24.67 23.03 23.10  Pt. 208°-212° C. under 10	2.74 2.66 2.06 1.82 1.57 1.06 0.75 0.30 0.51 0.25   o mm. mercury pressur fatty acid.
Oleonitrile. B.Pt. 2.  0 5 10 15 20 25 30 40 55 80 100  Methyl Oleate. B. 1 containin	10°-215° C. under 15 n  47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87 24.67 23.03 23.10  Pt. 208°-212° C. under 16 g o.84 per cent. of free	nm. mercury pressure.  2.74 2.66 2.06 1.82 1.57 1.06 0.75 0.30 0.51 0.25
Oleonitrile. B.Pt. 2	10°-215° C. under 15 n 47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87 24.67 23.03 23.10  Pt. 208°-212° C. under 16 g o.84 per cent. of free	nm. mercury pressure.  2.74 2.66 2.06 1.82 1.57 1.06 0.75 0.30 0.51 0.25   o mm. mercury pressure.
Oleonitrile. B.Pt. 2	10°-215° C. under 15 n  47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87 24.67 23.03 23.10  Pt. 208°-212° C. under 16 g o.84 per cent. of free	nm. mercury pressure.  2.74 2.66 2.06 1.82 1.57 1.06 0.75 0.30 0.51 0.25   Description of the control of the co
Oleonitrile. B.Pt. 2	10°-215° C. under 15 n 47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87 24.67 23.03 23.10  Pt. 208°-212° C. under 16 g o.84 per cent. of free	nm. mercury pressure.  2.74 2.66 2.06 1.82 1.57 1.06 0.75 0.30 0.51 0.25   o mm. mercury pressur fatty acid.  2.74 2.62
Oleonitrile. B.Pt. 2.  0 5 10 15 20 25 30 40 55 80 100  Methyl Oleate. B. I containin 0 5 20 35	215° C. under 15 n  47.89 28.71 27.02 26.45 27.99 26.64 25.25 24.87 24.67 23.03 23.10  Pt. 208°-212° C. under 10 g 0.84 per cent. of free  47.89 31.45 24.99 —	nm. mercury pressure.  2.74 2.66 2.06 1.82 1.57 1.06 0.75 0.30 0.51 0.25  0 mm. mercury pressur fatty acid.  2.74 2.62 2.39 1.83

of emulsions, especially in the case of oils and related compounds of high molecular weight, is clearly not determined simply by the magnitude of the interfacial tension and the formation of a stable adsorbed film at the interface. The cybotactic condition of the liquid to be dispersed is of equal importance in ordinary emulsification; while, in scouring processes, related adhesion phenomena acquire exceptional significance.

Since the difficulty of scouring mineral oil is to a large extent overcome by the addition of a small amount of oleyl alcohol, the properties of other mineral oil mixtures were investigated. The data are summar-

ised in Table III, illustrated by Figs. 3 and 4.

Despite the relatively high values of interfacial tension in the case of olive oil, oleonitrile and methyl oleate, these compounds are easily removed from wool by emulsification with soap and soda solution. Evidently they are not sufficiently polar for adhesion to become pronounced and prevent scouring, but differences in adhesion are revealed by the different concentrations necessary to promote the perfect scouring of mineral oil. In admixture with the latter, they function as diluents which are easily emulsified and can, in addition, reduce the oil-water interfacial tension to aid the removal of mineral oil. Oleonitrile appears to be the best of the three compounds, a perfect scour being realised with a mixture containing as much as 45 per cent. of mineral oil.

The case of oleic acid is peculiar. Besides being, in general, quite as effective as oleyl alcohol in reducing the oil-water interfacial tension, it has the additional merit of being easily removed from wool by means of soda solution. Oleic acid should therefore be even more effective than oleyl alcohol in promoting the removal of mineral oil from wool. Actually, in good agreement with Spennrath's 5 result, 70 per cent. of oleic acid is needed for the purpose, and it must function simply as a scourable diluent for mineral oil. The reason for its failure is the fact that it is converted into soap when scouring is commenced. In effect, it is removed to the water phase and interfacial tension is simply that of mineral oil against soap solution; whereas when oleyl alcohol is used, interfacial tension is reduced by alcohol in the oil phase as well as soap in the water phase. For this reason oleyl alcohol is highly effective. but it does not provide a perfect solution of the problem of removing mineral oil from wool. The best result, given by 6 per cent. of oleyl alcohol in admixture with mineral oil, is not sufficiently perfect to justify recommendation to the trade, even if the cost were satisfactory. Oleonitrile is also ineffective, because too high a concentration is needed to give perfect results. Some oil-soluble polar compound, intermediate in polarity between oleyl alcohol and oleonitrile is required, and its discovery will solve the problem of providing the worsted trade with a completely stable oil possessing perfect scouring properties.

Textile Chemistry Laboratory, The University, Leeds.

<sup>&</sup>lt;sup>5</sup> Spennrath, quoted by O. Walther, Färber Zeitung, 99, 1892-93.

#### GENERAL DISCUSSION.

**Professor Krais,** in introducing his paper for discussion, said that most of the difficulties could now be overcome by boiling-out the goods before dyeing. By this process the inequalities are diminished or disappear altogether.

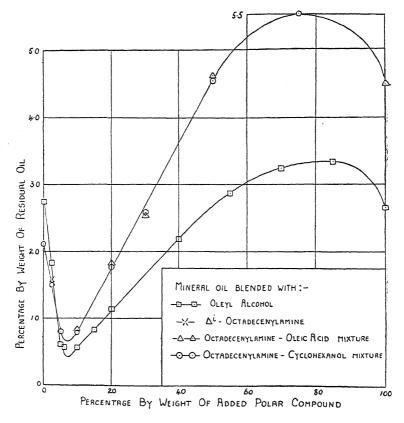
Dr. Speakman, in introducing his paper for discussion, said: The fact that adhesion phenomena play a large part in determining the difficulty of removing oils from wool was deduced mainly from the properties of oleyl alcohol-mineral oil mixtures. For the argument to be entirely convincing, it is necessary to show that the phenomena observed with oleyl alcohol are not peculiar to this compound. Experiments were therefore carried out with mixtures of mineral oil and  $\Delta$ -i-octadecenylamine (B.P. 200°-210° C. at 17 mm.). The amine is solid at 25° C. and tends to separate from solution in mineral oil at room temperature, especially when present in high concentration. To overcome the difficulty, 5 per cent. by weight of oleic acid or cyclohexanol was added to the mixtures containing large amounts of the amine. Actually, the device proved to be quite unnecessary because sufficient oleic acid for the purpose of preventing separation of amine is adsorbed from the soap solution used in scouring. The wool was oiled, as before, with 5 per cent. by weight of the amine or its mixture with oleic acid or cyclohexanol, and the oil retained after scouring estimated by ether extraction. A summary of the data obtained is given in the table.

Per Cent. by Weight of Added Polar	Residual Oil—Per Cent. on Weight of Wool Oiled with:—					
Compound or Mixture.	Amine.	Amine-cyclohexanol Mixture.	Amine-oleic Acid Mixture.			
0•0 2•5 5•0	2·74 1·32	1·26 0·79				
10.0		0.78	o-81			
20.0	No. of Contract of	1.78	1.83			
30.0		2.61	2.55			
50.0	and the same of th	4.56	4.62			
75.0		5.21	-			
100.0	, ,		4.49			
í		1				

A blank experiment in which the fabric was oiled with mineral oil containing 5 per cent. by weight of cyclohexanol, showed that 2·10 per cent. of oil is retained after scouring. The marked similarity in the influence of the amine and oleyl alcohol on the scouring of mineral oil is illustrated by the figure. Actually, adhesion phenomena are far more pronounced in the case of the amine, none of the mixture containing 75 per cent. of this compound being removed in the scouring process. It should perhaps be explained that more oil (5·5 per cent.) is extracted from the cloth than was applied (5·0 per cent.) because fatty acid is adsorbed from the soap solution.

In the paper, attention has been restricted to the properties of well-defined chemical compounds, none of which provides a perfect solution

of the technical problem of conferring emulsifiability on mineral oil. As this might lead to the assumption that the problem is still unsolved, it is necessary to state that a mixture of mineral oil and 15 per cent. of wool fat ethers has been found to scour with as much ease as olive oil. The mixture is non-oxidising and inexpensive, so that there appears to be no reason why it should not displace olive oil for use on worsteds.



Finally, in a study of the carcinogenic potency of mineral oils, Twort has shown that the addition of glycerides reduces their potency, although no oil surpasses lanolin in this respect. There is a close parallel between these results and those discussed in the above paper. Mineral oil is extremely difficult to remove from wool by emulsification, whereas mixtures with glycerides such as olive oil are removed more readily. Although no results are quoted for lanolin-mineral oil mixtures, lanolin is known to be even more effective in facilitating the scouring of mineral oil. So far, the alcohols have not been used as agents for reducing the carcinogenic potency of mineral oils, but there can be little doubt that such polar compounds will reduce the risk of cancer formation by promoting emulsification: an oil which is easily and completely removed from the skin must carry less risk than one which is difficult to emulsify. Polar compounds, in admixture with mineral oil, may, however, function as anti-carcinogenic agents in yet another

way. It is known that the carcinogenic agents of mineral oil are associated with unsaturated compounds which are free to concentrate at any surface to which the oil is applied, the non-polar paraffin molecules offering little or no resistance. When, however, oil-soluble polar compounds, such as oleyl alcohol or wool fat ethers, are mixed with mineral oil, their polar character is sufficiently well-marked to cause strong concentration at the surface, and the less polar, unsaturated hydrocarbons, which are carcinogenic, are excluded. Thus the addition of polar compounds to mineral oil will reduce its carcinogenic potency in two ways: by conferring emulsifiability on the oil to facilitate its removal from the skin; and by preventing access of the carcinogenic agent to the skin. Experiments to test the validity of this view have been undertaken by Professor R. D. Passey, Director of Cancer Research of Leeds University.

**Professor P. Krais** (*Dresden*) said: Dr. Speakman's work is very important, and we are making endeavours on similar lines. It must be remembered that an easy removal of oils and fats from textiles is of importance, not only for lubricated wool fibres, but in every case where lubricants of any kind are used and get into the goods.

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#### THE PHOTO-REACTIONS OF OXALATES WITH BROMINE AND WITH IODINE. PART I.— EXPERIMENTAL.

By Robert Owen Griffith, Andrew McKeown, and Albert GORDON WINN.

# Received 7th November, 1932.

In their well-known work, Berthoud and Bellenot 1 have elucidated the main features of the photo-oxidations of neutral oxalates by bromine and by iodine. The most significant result accruing from their work is that the rates of these reactions are proportional to the square root of the absorbed energy, and later work by others 2 has amply confirmed this fact. They infer that the reaction mechanism in both cases involves bromine (or iodine) atoms formed as a result of primary photodissociation.

The original intention of the present investigation was to study the photo-oxidation of oxalic acid by bromine, a reaction which has hitherto only been dealt with qualitatively (cf. Roloff 3). It soon became evident, however, that here we are dealing with two simultaneous and independent processes, the one involving the  $HC_2O_4^-$  ion and the other the  $C_2O_4^{--}$ ion. It was therefore found necessary to extend the investigation over the whole range of oxalate mixtures from neutral oxalate to oxalic acid. In the photo-reaction between bromine and neutral oxalate, Berthoud and Bellenot's measurements have been confirmed, but we have also extended the data by studying the effect of light of different wavelengths and particularly by studying the retardation by bromide at different wavelengths. These additional results are of particular significance for the interpretation of the reaction. Finally, it has been sought to apply the reaction mechanism which we suggest for the bromine-oxalate reaction to the corresponding reaction with iodine. For this purpose it has been necessary to extend the existing data for the latter reaction to regions of very low concentrations of the retarding iodide ion. In the present paper are presented the experimental results which we have obtained for the three photo-processes: (a) bromine and HC2O4ion; (b) bromine and  $C_2O_4$ —ion; and (c) iodine and  $C_2O_4$ —ion. Their theoretical interpretation is discussed in the paper which follows (p. 386).

# Experimental.

A plan of the apparatus is given in Fig. 1. The light source was a quartz mercury lamp (burning at 150 volts and 3.8 amps.) of straight

7, 307, 1924.
<sup>2</sup> Briers, Chapman, and Walters, *J.C.S.*, 562, 1926. Allmand and Young, Trans. Faraday Soc., 27, 515, 1931.

3 Roloff, Z. physikal. Chem., 13, 346, 1894.

<sup>&</sup>lt;sup>1</sup> Berthoud and Bellenot, J. Chim. physique, 21, 308, 1924; Helv. Chem. Acta,

tube pattern with a plane window at the anode end. The remainder of the apparatus (with the exception of the two large screens  $S_3$  and  $S_4$ ) was mounted on an optical bench. The screens were water-cooled and fitted with water-cooled shutters. The lenses in C, and the lenses  $L_1$ ,  $L_2$ ,  $L_3$  were of quartz, the object of the last of these ( $L_3$ ) being to bring the light transmitted by the reaction cell to a sharp focus on the thermopile P. Filter vessels containing liquid filters, coloured glass filters and neutral filters were mounted in front of the diaphragm  $D_1$ . The reaction cells were permanently clamped into cylindrical jackets (for controlling the temperature) which sat accurately in a cradle. The cradle was fitted with various controls, which made it possible to adjust the position of the cell so that its axis coincided with the axis of the beam, and also ensured that once the position had been fixed it was always

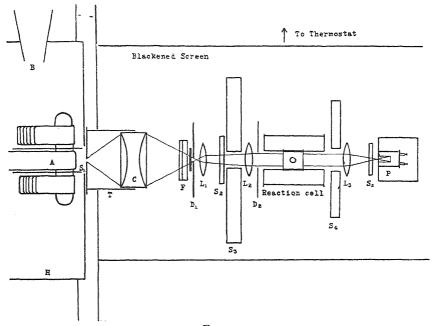
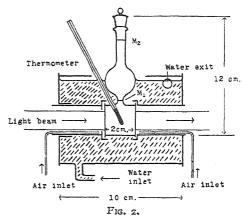


Fig. 1.

possible after removing the cell to replace it in exactly the same position. Temperature control of the reaction mixture was obtained by pumping water from a thermostat into the cell jacket, whence it flowed back to the thermostat. Two cylindrical reaction cells made of quartz with plane parallel end-plates were used, the one 2 cm. in length, the other 10 cm. The former with its temperature jacket is depicted in Fig. 2; the other was essentially similar in construction. The object of the sidearm with bulb was to permit withdrawal of samples for analysis from the cell itself both before and after illumination. This procedure involves the application of small but definite corrections for the loss of bromine into the dead-space which results from the withdrawal of the initial sample. Since, for the experiments with bromine, the working temperature was usually below that of the room, precautions had to be taken to prevent the formation of dew on the end-plates of the reaction cells. This was done by blowing dry air against them.

The energies of (a) the incident and (b) the transmitted beams were measured with a Moll large-surface thermopile in conjunction with a

Moll galvanometer; (a) with the reaction cell containing water, and (b) with the cell containing reaction mixture. The thermopile was fitted with a blackened "stop" as recommended by Allmand and Beesley 4 and with a quartz window, and the whole was placed in a box heavily lined with felt. The thermopile - galvanometer combination was calibrated by means of a carbonfilament lamp standardised by the National Physical Laboratory, and also with a standard Hefner lamp.



Re-calibration at the end of the whole series of measurements showed good agreement with the former calibration. For experiments with high intensities it was necessary to reduce the sensitivity of the thermopile-galvanometer combination; this was done by inserting a resistance in series with the galvanometer. Using the method suggested by Forbes,<sup>5</sup> a linear relation between incident intensity and galvanometer deflection was shown to be applicable up to an intensity of at least 25 H.K. Corrections were applied in the calculations of quantum yields for losses due to reflection at quartz-air surfaces. For experiments in which the light absorption was less than 30 per cent., the energy absorbed was calculated from the incident intensity together with the appropriate extinction data (cf. footnote, p. 378).

Experiments have been carried out using light of wavelengths 579, 546, 436, 405, 365 and 313  $\mu\mu$ . The following filters were used:—

For 579  $\mu\mu$ : 2 cm.  $2\frac{1}{2}$  per cent. CuCl<sub>2</sub> solution + Schott glass filter O.G. 2 (2 mm.). Transmission at 579  $\mu\mu$  = 45 per cent.

For 546  $\mu\mu$ : 2 cm.  $2\frac{1}{2}$  per cent. CuCl<sub>2</sub> solution + Kodak green line monochromat No. 77 A. Transmission at 546  $\mu\mu$  = 53 per cent.

For 436  $\mu\mu$ : 2 cm.  $2\frac{1}{2}$  per cent. CuCl<sub>2</sub> solution + Schott glass filter B.G. 12 (1 mm.) or Schott B.G. 1 (2 mm.) + 1 cm. 2 per cent. quinine sulphate solution. Transmission at 436  $\mu\mu$  = 51 per cent.

For  $405 \mu\mu$ : 2 cm.  $2\frac{1}{2}$  per cent. CuCl<sub>2</sub> solution + 1 cm. 0·1 per cent. quinine sulphate solution + 5 mm. 0·02 per cent. diamant fuchsin. Transmission at  $405 \mu\mu$  = 16 per cent. 6

For 365  $\mu\mu$ : Schott glass filter U.G. I (2 mm.) + Schott B.G. I2 (1 mm.). Transmission at 365  $\mu\mu$  = 50 per cent.

For 313  $\mu\mu$ : 2 cm.  $2\frac{1}{2}$  per cent. CuSO<sub>4</sub> solution + 5 mm. 0 o2 per cent. K<sub>2</sub>CrO<sub>4</sub> solution + Schott U.G. 2 (1 mm.). Transmission at 313  $\mu\mu$  = 13 per cent.

<sup>&</sup>lt;sup>4</sup> Allmand and Beesley, J.C.S., 2693, 1930. <sup>5</sup> Forbes, J. Physical Chem., **32**, 482, 1928.

<sup>&</sup>lt;sup>6</sup> The light transmitted by this filter contains about 12 per cent. of 436  $\mu\mu$ .

The liquid filters in the above list were contained in glass cells, except for the isolation of the 313  $\mu\mu$  line when quartz cells were used. Variation of the light intensity was effected by inserting one or more of a series of neutral filters.

The chemicals used were A.R. preparations, supplied by Merck. Kahlbaum, and Hopkin and Williams. The extent of reaction was determined by estimating the initial and final concentrations of bromine (or iodine) by running the sample into sodium arsenite solution (containing excess NaHCO<sub>3</sub>) and back-titrating with iodine using starch as indicator. With suitable precautions the method is accurate for the estimation of very low concentrations of the halogen (below M/1000). In the calculation of the quantum yields for the photo-reaction between bromine and oxalic acid or oxalates, it is necessary to subtract from the observed extents of reaction the contributions made by the simultaneously occurring thermal reaction. These latter were computed from the data of Griffith, McKeown, and Winn.7 It is to be noted that correction in this manner assumes additivity of the thermal and photo-processes. i.e. that neither reaction affects the other. This assumption can hardly be in serious error, since (a) in practically all our experiments the thermal correction is only a few per cent. (usually less than 5 per cent.) of the total change, and (b) the mechanisms of the thermal and photo-processes are entirely different. For the iodine reaction, the thermal correction was in all cases small enough to be neglected.

For each reaction mixture two or more experiments with different times of illumination were carried out. For the bromine reactions most of the experiments were carried out at 11.5°; for the iodine reaction at 25°.

# Experimental Data.

In what follows the following symbols are used:—

 $\Sigma[\mathrm{Br_2}]_0 = \mathrm{initial}$  concentration of total titratable bromine (moles/litre).

x = extent of photochemical reaction (after correction for the thermal reaction) (moles/litre).

t = time of illumination (minutes).

c = percentage thermal correction = 100 x (thermal)/x (total).

 $\theta = \text{temperature}.$ 

l = length of reaction cell (cm.).

 $A_m$  = mean percentage light absorption during the experiment. E = rate of absorption of radiant energy in quanta per c.c.

of beam per min.

 $\gamma =$  quantum yield.

# I. THE PHOTO-REACTIONS OF BROMINE WITH OXALIC ACID AND WITH NEUTRAL OXALATE.

# (A) Variation of the Incident Intensity.

The results summarised in Tables I. and II. show that under otherwise identical conditions the quantum yield  $(\gamma)$  of both reactions is inversely proportional to the square root of the rate of quantum absorption (E). Thus,  $\gamma$  is inversely proportional to the square root of the incident

<sup>&</sup>lt;sup>7</sup> Griffith, McKeown, and Winn, Trans. Faraday Soc., 28, 107, 1932.

TABLE I: Reaction Mixture = M/8 H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + M/32 KBr + M/600 Br<sub>2</sub>.  $\theta = \text{II:}5^{\circ}.$ 

t.	x. 104.	с.	A m.	E. 10 <sup>-16</sup> .	γ.	$\gamma \sqrt{E} \cdot 10^{-7}$ .			
		$\lambda = 9$	546 μμ; l =	10 cm.					
45 40 90	2*42 2*08 1*98	12.0 12.2 21.2	14.3 14.3	0.644 0.252 0.114	0.80 0.86 1.84	6°4 6°5 6°2			
		$\lambda = \lambda$	436 $\mu\mu$ ; $l=$	Io cm.					
20 20 35 60 90	5.04 4.11 4.81 5.09 4.85	3°5 4°9 5°7 8°0 11°3	100 100 100	3.51 2.41 1.08 0.418 0.153	0.68 0.81 1.21 1.93 3.34	12.7 12.6 12.5 13.0			
	$\lambda = 365 \ \mu\mu$ ; $l = 2 \ \text{cm}$ .								
12 20 35	5°11 4°95 4°79	2·3 3·4 4·6	85·5 88·3 87·2	12.4 4.58 1.36	0°57 0°96 1°67	20.0 19.8 19.2			

TABLE II.  $\theta = 6.5^{\circ}; \ l = 2 \text{ cm}.$ 

t.	x.104.	c.	A <sub>m</sub> .	E.10 <sup>-16</sup> .	γ.	$\frac{\gamma \sqrt{E} \cdot 10^{-10}}{\left[C_2 O_4\right]_m}.*$
	M/20 K	$C_2C_2O_4 + M/2$	2 KBr + M/0	500 Br <sub>2</sub> . λ=	= 546 μμ.	
20 35 59	4.20 5.00 5.13	3.8 4.4 6.0	1•66 1•54 1•47	0°294 0°095 0°034	33.1 10.3 10.5	1.13 1.21 1.25
	M/100	$K_2C_2O_4 + M$	/4  KBr + M	/600 Br <sub>2</sub> . λ	$= 436 \mu\mu$ .	
10 24 40	4.00 5.28 5.30	2.7 3.0 4.0	60°8 58°4 57°6	7*36 2*61 0*95	0°71 1°16 2°02	1.96 1.94 2.04
	M/100  K	$C_2C_2O_4 + M/$	4 KBr + M/	1200 Br <sub>2</sub> . λ	$= 365 \mu\mu$ .	
8 16 28	3.89 4.31 4.49	1*2 1*4 1*8	75°2 75°4 72°8	7°73 2°38 0°94	0.82 1.48 2.23	2*34 2*34 2*22

energy, and the relation holds at the three wavelengths studied. This result is in agreement with Berthoud and Bellenot, who observed the same dependence of the rate on incident intensity for the case of the neutral oxalate reaction in white light.

<sup>\*</sup>Since the concentration of the oxalate falls slightly during an experiment,  $\gamma\sqrt{E}$  is divided by the mean value of  $[C_2O_4--]$ . This applies to all experiments with neutral oxalate.

## (B) Variation of the Concentration of Bromine.

The effect of bromine concentration on the rate of the oxalic acid reaction has been studied at the five wavelengths 546, 436, 405, 365 and 313  $\mu\mu$ , with the reaction mixture M/8  $H_2C_2O_4+M/32$  KBr and varying the bromine concentration between M/300 and M/5000. The results obtained show that the product  $\gamma\sqrt{E}$  is dependent on the absorption of the reaction mixture, but that it is constant over a considerable range of absorption extending to about 85 per cent. Within this range  $\gamma\sqrt{E}$  is independent of (i) the initial concentration of bromine, (ii) the extent of reaction, and (iii) the dimensions of the reaction cell. Table III. gives the results obtained for the reaction mixture M/8  $H_2C_2O_4+M/32$  KBr + bromine at II·5° with light of 436  $\mu\mu$ . The results obtained with the other wavelengths (omitted to save space) were similar, except that at 313  $\mu\mu$  it was impossible to obtain incomplete absorption owing to the very high extinction of the solution.

TABLE III.  $\mbox{Variation of Concentration of Bromine.}$   $M/8~H_2C_2O_4+M/32~\mbox{KBr}+\mbox{Br}_2.$   $\theta=\mbox{11}^{\circ}5^{\circ}.$   $\lambda=436~\mu\mu.$ 

∑[Br <sub>2</sub> ] <sub>0</sub> ×10 <sup>4</sup> .	l.	t.	x. 104.	c.	A <sub>m</sub> .	E.10-16.	γ.	$\gamma \sqrt{E}$ . ro $-7$ .
31.9 31.2 29.9 17.38 17.02 16.49 14.61 9.87 9.65 9.35 16.82 16.98 16.42 16.61 8.52 8.42	10 10 10 10 10 10 10 10 10 10 2 2 2 2 2	30 60 90 10 20 30 50 8 16 24 12 16 24 12 16 24 24	5'3 11'4 18'7 1'91 4'11 6'25 11'75 2'07 4'02 5'75 3'12 4'59 6'05 9'07 2'27 4'34	9°0 6°2 4°4 7°7 4°9 3°8 2°0 3°7 2°2 1°7 3°9 3°6 3°0 2°8 3°0	100 100 100 100 100 97 83 87.5 79.4 59.4 60.6 56.7 48.0 30.1 29.3	3·16 3·28 3·36 2·45 2·41 2·38 2·91 3·11 2·99 2·70 9·69 7·45 9·46 5·78 5·20 4·85	0.53 0.55 0.59 0.74 0.81 0.77 0.79 0.80 0.84 0.43 0.50 0.44 0.50 0.60 0.60	9'4 10'0 10'8 11'6 12'6 12'8 13'1 13'9 13'8 13'4 13'7 13'6

Mean of last nine = 13.7

If we define the "extinction" of the reaction mixture as the quantity  $\alpha$ .  $\mathcal{Z}[\mathrm{Br_2}]_m$ . l, where  $\alpha$  is the extinction coefficient  $\left(\alpha = \frac{\log_e I_0/I}{\mathcal{Z}[\mathrm{Br_2}] \cdot l}\right)$ , it is possible to show that the observed variation of  $\gamma \sqrt{E}$  with the extinction is a systematic one. Thus in Fig. 3, the ratio of  $\gamma \sqrt{E}$  for a given extinction to the limiting value of  $\gamma \sqrt{E}$  for weak absorption is plotted against the function  $\alpha$ .  $\mathcal{Z}[\mathrm{Br_2}] \cdot l$ . It is seen that the points obtained from results at three different wavelengths (436, 405, and 365  $\mu\mu$ ) lie on a single curve, showing that the ratio  $\frac{\gamma \sqrt{E}}{\gamma \sqrt{E}}$  (limiting) is a function only of the extinction, and not of the wavelength used.

This result can be readily explained on the basis of a generalised mechanism of the simplest type for a photo-reaction with rate propor-

tional to  $I_0^*$ . Thus for a halogen  $X_2$  and an acceptor  $A^-$ , we postulate a mechanism of the type (1)  $X_2 + h\nu \to 2X$ , (2)  $X + A^- \to X^- + A$ , (3)  $X_2 + A \to \text{resultants}$ , (4)  $X + X \to X_2$ . From this may easily be deduced the equation:

$$\gamma \sqrt{E} = 2k_2 \sqrt{\frac{k_1}{k_4}} [\mathbf{A}^-] \frac{\mathbf{I} - e^{-\mathrm{cal}/2}}{\sqrt{\mathbf{I} - e^{-\mathrm{cal}}} \sqrt{c\alpha} l'}$$

in which c is the concentration of  $X_2$  (i.e.  $\Sigma[X_2]$ ). Putting  $c\alpha l = y$ , we have:

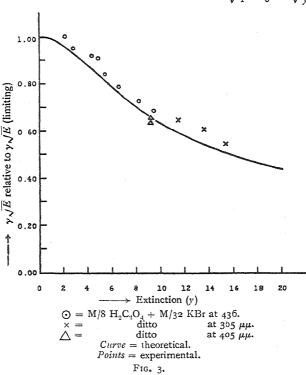
$$\gamma\sqrt{E} = 2k_2\sqrt{\frac{k_1}{k_4}}[A^-]\frac{I - e^{-y/2}}{\sqrt{I - e^{-y}}\sqrt{y}} \qquad . \tag{I}$$

It is to be noted that E is defined as the rate of absorption in quanta per c.c. of beam per minute, for in this way the product  $\gamma\sqrt{E}$  is made independent of the cross-section of the beam and of the length of the

reaction cell. Table IV. gives the value of the function  $\frac{1 - e^{-y/2}}{\sqrt{1 - e^{-y}}\sqrt{y}}$ 

various values of y; the second column gives the percentage absorptions corresponding tο these same values of y, and the last column | o 60 gives the value of  $\gamma\sqrt{E}$  obtained from equation (1) relative to  $\gamma\sqrt{E}$ corresponding to y = 0, i.e., the limit of very weak absorption.

It is seen that  $\gamma\sqrt{E}$  is practically constant from  $\gamma=0$  to  $\gamma=1.8$ , the slight fall which occurs over this range being within



the experimental error of measurement of  $\gamma\sqrt{E}$ , namely about 3 per cent. For values of  $\gamma$  above I·8, however, the value of  $\gamma\sqrt{E}$  falls rapidly. The latter figure  $\gamma=1.8$  corresponds to an absorption of 83·5 per cent., so that up to about 85 per cent. absorption  $\gamma\sqrt{E}$  should be practically constant, which is in complete agreement with the experimental findings. Further, equation (I) shows  $\gamma\sqrt{E}$  to be independent of the dimensions of the reaction cell except in so far as l determines the extent of absorption, so that  $\gamma\sqrt{E}$  is completely independent of l for absorptions below

<i>y</i> -	(Per Cent.).	$\frac{1 - e^{-y/2}}{\sqrt{1 - e^{-y}}\sqrt{y}}$	$\gamma \sqrt{E}$ . (Relative).	3'-	(Per Cent.).	$\frac{1 - e^{-y/2}}{\sqrt{1 - e^{-y}}\sqrt{y}}.$	$\gamma\sqrt{E}$ . (Relative).
0.0 0.2 0.4 0.6 0.8 1.4 1.8	0 18·1 33·0 45·1 55·1 75·3 83·5	0.500 0.500 0.499 0.498 0.497 0.490 0.484	1.000 1.000 0.998 0.996 0.994 0.980 0.968	2.4 3.0 5.0 10.0 14.0 20.0	90.9 90.9	0'473 0'460 0'412 0'314 0'267 0'224	0'946 0'920 0'824 0'628 0'534 0'448

TABLE IV.

about 85 per cent. The calculated figures in Table IV. have been plotted in Fig. 3 for quantitative comparison with the experimental data. The agreement is good, considering that the reaction mixtures were not stirred; the fact that all the experimental points lie somewhat above the theoretical curve may be attributed to the fact that the concentration of bromine in the light beam was always below the mean concentration from which the extinction was calculated. The predictions of the generalised chain mechanism are thus in complete accord with the experimental facts.

It will be appreciated that any attempt to investigate the dependence of the quantum yield  $(\gamma)$  on the other variables must be carried out within the region of constancy of  $\gamma\sqrt{E}$ . Thus, owing to the possibility of a change of a with the concentration of bromide in the system, any attempt to determine the effect of bromide concentration on y under conditions such that the absorption is greater than 85 per cent. may lead to entirely erroneous results, due to a change with [Br-] of the variable  $\alpha \cdot \Sigma[\operatorname{Br}_2]_m \cdot l$ . It is for this reason that practically all the experimental data which follow refer to very low concentrations of bromine, so that all comparisons are made between values of  $\gamma\sqrt{E}$  within its range of non-dependence on extinction. The necessity for the general recognition of some constant characteristic of an  $I_0^{\frac{1}{2}}$  reaction, in the same way as the quantum yield is characteristic of a reaction proportional to the first power of the incident intensity, has been recognised by Allmand.8 It would appear that the function  $\gamma\sqrt{E}$  corresponding to an absorption below about 85 per cent. adequately fulfils this requirement. For the interpretation of the remaining kinetic data, therefore, this quantity has been used as a function dependent solely on the variables (a) wavelength of light, (b) concentration of oxalate, (c) concentration of bromide, and (d) temperature.

For the reaction of bromine with neutral oxalate, the dependence of  $\gamma\sqrt{E}$  on the concentration of bromine has only been tested for conditions such that the absorption is less than 85 per cent. In this range, in agreement with the behaviour of the oxalic acid reaction,  $\gamma\sqrt{E}$  is found to be independent of  $\Sigma[Br_2]$ .

### (C) Variation of the Wavelength $(\lambda)$ of the Incident Light.

In the case of the oxalic acid reaction, the reaction mixture M/8  $H_2C_2O_4 + M/32$  KBr + Br<sub>2</sub> has been studied at 11.5° at five wavelengths. The results are summarised in Table V.

<sup>&</sup>lt;sup>8</sup> Allmand, J.C.S., 1557, 1929.

-		~	-	*	~ ~
.1.	А	B	1.	Η.	V.

) ()	546	436	405	365	313
$\lambda (\mu \mu)$ $\gamma \sqrt{E}$ . 10 <sup>-7</sup> .	6.0	13.7	16.2	20.3	24'I
$\gamma\sqrt{E}$ relative to	1.0	2.3	2°75	3.4	4.0
value at 546 μμ					

For the neutral oxalate reaction, it was not found possible to study any single reaction mixture at all these five wavelengths, but two overlapping series at 6.5° with different bromide concentrations give the desired data, as shown in Table VI.

TABLE VI.

[Bromide].	$\gamma\sqrt{E}$ . 10 $^{-10}/[{ extsf{C}_2 extsf{O}_4}^{}]_m$ .						
	579-	546.	436.	405.	365 μμ.		
M/2	0.94	1.11	1.67	_	1.83		
$M/_4$	_	1.10	1.98	1.99	2.33		

It would appear that the increase of  $\gamma\sqrt{E}$  on decreasing the wavelength is much less rapid for the neutral oxalate reaction than for the oxalic acid reaction. That this is not an essential difference between the two reactions, however, but is due to the fact that the two variations of  $\gamma\sqrt{E}$  with  $\lambda$  refer to different bromide concentrations is shown by the data in Table VII. In this Table the values of  $\gamma\sqrt{E}$  given are not absolute values, and are comparable only for a given reaction mixture at the three different wavelengths. It will be seen that the increase of  $\gamma\sqrt{E}$  with decreasing  $\lambda$  is dependent on the bromide concentration. It is greatest at low bromide concentrations, but for a given value of [Br-] the increase is the same for both the oxalic acid and neutral oxalate reactions.

TABLE VII.

Oxalate.	[KBr],	γ√E at 365 μμ.	γ√Ē at 436 μμ.	γ√E at 546 μμ.	$\frac{(\gamma\sqrt{E})_{365}}{(\gamma\sqrt{E})_{436}}$	$\frac{(\gamma \sqrt{E})_{436}}{(\gamma \sqrt{E})_{546}}$	K <sub>3</sub> 6 <sub>5</sub> K <sub>43</sub> 6	K436 K546
$K_{2}C_{2}O_{4}$ $K_{2}C_{2}O_{4}$ $K_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $K_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$ $H_{2}C_{2}O_{4}$	$M/2 \\ M/4 \\ M/4 \\ M/8 \\ M/8 \\ M/8 \\ M/16 \\ M/32 \\ M/64$	1.83 2.33 2.27 3.02 3.93 7.15 13.3	1.67 1.98 1.94 2.43 3.26 5.42 9.27 15.3	4.00	1°10 1°18 1°17 1°24 1°21 1°32 1°44 1°58	1·50 1·80 — — — — 2·28	1.07 1.12 1.11 1.12 1.09 1.10 1.08	1°34 1°47 — — — 1°32

It is possible to account quantitatively for this variation of  $\frac{(\gamma\sqrt{E})_{\lambda_1}}{(\gamma\sqrt{E})_{\lambda_2}}$  with [Br-] by assuming that the kinetic equation for both reactions contains the term  $\frac{1}{\sqrt{[\mathrm{Br}^-]+K_3\frac{\alpha_1}{\alpha_2}}}$  where  $\alpha_1$  is the extinction coefficient

of  $Br_2$  molecules,  $\alpha_2$  the extinction coefficient of  $Br_3^-$  ions, and  $K_3$  the equilibrium constant of tribromide formation  $\left(K_3 = \frac{[Br_2][Br^-]}{[Br_3^-]}\right)$ . Thus, let

$$(\gamma\sqrt{E})_{\lambda} = \frac{K_{\lambda}}{\sqrt{[\mathrm{Br}^{-}] + K_{3}\frac{\alpha_{1}}{\alpha_{2}}}} \quad . \quad . \quad (2)$$

where  $K_{\lambda}$  includes those quantities which vary with  $\lambda$  but are independent of [Br-]. Table VIII. gives the values of  $\alpha_1$ ,  $\alpha_2$  and  $K_3 \frac{\alpha_1}{\alpha_2}$  at various wavelengths. Application of equation (2) to the values of  $\gamma \sqrt{E}$  given

 $(\lambda \mu \mu)$ 436 365 289 546 405 313 579 128 164 120 860 7900 454  $K_3 \cdot \alpha_1/\alpha_2$ 0.183 0.040 0.010 0.0003

TABLE VIII.

in Table VII. yields the values of the ratio  $K_{\lambda_1}/K_{\lambda_2}$  given in the last two columns of this Table. It will be seen that over the whole range of bromide studied (M/2-M/64),  $K_{\lambda_1}/K_{\lambda_2}$  is a reasonably good constant, showing that the effect under consideration is adequately interpreted

by a term 
$$\frac{1}{\sqrt{[\mathrm{Br}^-]+K_3\frac{\alpha_1}{\alpha_0}}}$$
 in the kinetic equation for both reactions.

## (D) Variation of the Concentration of Neutral Oxalate and of Oxalic Acid.

(a) Neutral Oxalate Solutions.—The results of 10 insolations at 6.5° using solutions containing M/4 KBr + M/600 Br $_2$  with  $\lambda =$  546  $\mu\mu$  and using solutions containing M/2 KBr + M/600 Br $_2$  with  $\lambda =$  436  $\mu\mu$  show that  $\gamma\sqrt{E}$  is directly proportional to the concentration of neutral oxalate (K $_2$ C $_2$ O $_4$ ) over the range M/25 to M/200. Since this is in agreement with Berthoud and Bellenot, who studied the effect of this variable over the concentration range M/2-M/8 with white light, we may here refrain from publishing our data in detail.

The values of  $K_3$  are those obtained by Griffith, McKeown, and Winn (Trans. Faraday Soc., 28, 101, 1932). Values of  $\alpha_{\rm Br_2}$  and  $\alpha_{\rm Br_3}$ —were obtained by measurement of the extinctions of aqueous bromine solutions and of solutions of bromine in aqueous KBr. The figures given are molecular extinction coefficients to the base 10. They were determined at room temperature using Scheibe cells, (a) for the visible wavelengths with the Nutting photometer, and (b) in the ultra-violet by the sector-photographic method. The extinction measurements are not claimed to be of special accuracy, but may be regarded as sufficiently accurate for the purpose in view, viz, the determination of the magnitude of the term

$$\sqrt{\frac{\frac{1}{[Br^-] + K_3 \frac{\alpha_1}{\alpha_2}}}{\text{to within 2 or 3 per cent.}}}$$

( $\beta$ ) Solutions containing Neutral Oxalate, Acid-Oxalate, and Oxalic Acid.—Table IX. gives the variation of  $\gamma\sqrt{E}$  for a series of oxalate solutions of increasing [H+], ranging from neutral oxalate with a  $p_{\rm H}$  about 7 to a solution containing oxalic acid + HBr with a  $p_{\rm H}$  of less than 1. The whole series was effected with M/4 bromide and  $\lambda=436~\mu\mu$  at 11.5°. The Table gives also the compositions of these solutions, i.e., the concentrations of  $C_2O_4^{--}$ ,  $HC_2O_4^{--}$ , and  $H^+$ , calculated using the values of  $K_1$  and  $K_2$  (the two ionisation constants of oxalic acid) obtained by Griffith, McKeown, and Winn.

TABLE IX.

oxalate.	[C <sub>2</sub> O <sub>4</sub> ].	[HC <sub>2</sub> O <sub>4</sub> ].	(H <sup>1</sup> ).	$\gamma\sqrt{E}$ . 10 $^{-7}$ .	$\gamma \sqrt{E} \cdot 10^{-8}$ [HC <sub>2</sub> O <sub>4</sub> ] + 100[C <sub>2</sub> O <sub>4</sub> "].	Percentage C <sub>2</sub> O <sub>4</sub> Reaction.
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.00978 0.00448 0.000813 0.00021 0.000021		circa 10 <sup>-7</sup> 2.64 × 10 <sup>-3</sup> 1.42 × 10 <sup>-2</sup> 4.13 × 10 <sup>-2</sup> 2.78 × 10 <sup>-1</sup>	28·3 14·0 3·86 1·94 0·76	2·9 2·8 2·8 3·1 2·5	100 89 60 34 7

These results are most easily interpreted by the assumption that in all solutions more acid than neutral oxalate solutions, two independent photo-processes are occurring, the one with  $HC_2O_4^-$  ions, the other with  $C_2O_4^-$  ions, the latter being intrinsically much the more rapid. It is unnecessary to assume that  $H^+$  has any specific effect other than that of altering the ratio  $\frac{[HC_2O_4^-]}{[C_2O_4^-]}$  in the solution. Analysis of the above figures on this basis shows that the intrinsic rate of the  $C_2O_4^-$  reaction is about 100 times that of the  $HC_2O_4^-$  reaction in the presence of M/4 bromide. Column 6 of Table IX. gives the values of  $\frac{\gamma\sqrt{E}}{[HC_2O_4^-]}$ , which on this basis should be constant, and

 $[HC_2O_4^-] + 100[C_2O_4^{--}]$ , which on this basis should be constant, and the last column gives the extent of the " $C_2O_4^-$  reaction" as a percentage of the total reaction. It will be seen that it occurs to an appreciable extent even with the reaction mixture M/8  $H_2C_2O_4 + M/4$  HBr in which the concentration of  $C_2O_4^-$  ions is as low as  $2 \times 10^{-5}$ .

(y) Oxalic Acid Solutions.—The results of Table IX. refer to solutions M/4 with respect to bromide. In Table X. are summarised values of  $\gamma\sqrt{E}$  for oxalic acid solutions of varying concentration in solutions M/32 with respect to bromide. The wavelength and the temperature are again  $436~\mu\mu$  and  $11.5^{\circ}$  respectively. The calculated concentrations of  $HC_2O_4^-$  and  $C_2O_4^-$  in these solutions are also given. Owing to the fact that the  $C_2O_4^-$  reaction has a much smaller retardation by bromide than has the  $HC_2O_4^-$  reaction (see page 381), the ratio of the intrinsic rates of the two reactions is a function of the bromide concentration. Combining the value of 100 obtained for this ratio at  $[Br^-] = M/4$  with the bromide retardations of the two reactions arrived at in section E, we calculate a value of 34 for the ratio of the rate of the

$\Sigma[H_2C_2O_4].$	[HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> ].	[C <sub>2</sub> O <sub>4</sub> ].	$\gamma \sqrt{E} \cdot 10^{-7}$ .	$\frac{\gamma\sqrt{E} \cdot 10^{-8}}{[\text{HC}_2\text{O}_4^-] + 34[\text{C}_2\text{O}_4^{}]}.$	Percentage [HC <sub>2</sub> O <sub>4</sub> <sup>-</sup> ] Reaction.
$M/8 \ M/16 \ M/32 \ M/64$	0.0656 0.0339 0.0234 0.0131	0.00014 0.00013 0.000112	13.9 9.3 6.2 3.8	2°0 2°1 2°2 2°2	93 90 84·5 77

TABLE X.

 ${
m C_2O_4}^--$  reaction to that of the  ${
m HC_2O_4}^-$  reaction at  $[{
m Br}^-]=M/32$ . The fifth column of Table X. gives the values of  $\frac{\gamma\sqrt{\bar E}}{[{
m HC_2O_4}^-]+34[{
m C_2O_4}^-]}$  which on this basis should be constant. It will be seen that for the reaction mixture M/8  ${
m H_2C_2O_4}+M/32$  KBr, with which the dependence of  $\gamma\sqrt{\bar E}$  on bromine concentration and on incident energy was studied (cf. Tables I. and III.), the  ${
m HC_2O_4}^-$  reaction is contributing 93 per cent. to the total measured reaction. The conclusions there drawn may therefore be regarded without serious error as referring to the pure  ${
m HC_2O_4}^-$  reaction.

#### (E) Variation of the Bromide Ion Concentration.

In the preceding section it has been shown that two reactions occur, the one a photo-oxidation of  $C_2O_4^{-}$ , the other of  $HC_2O_4^{-}$ . We now deal with the effects of bromide on the separate processes.

(a) The  $C_2O_4$ -- Reaction.—For the experiments carried out with neutral oxalate solutions it was shown in the last section that the measured reaction consists solely of the oxidation of  $C_2O_4$ -- ions. In Table XI. are given the bromide retardations experimentally observed at 6.5° for progressive doubling of the bromide concentration, i.e., the ratio of  $\frac{\gamma\sqrt{E}}{[C_2O_4--]_m}$  for a given bromide concentration to  $\frac{\gamma\sqrt{E}}{[C_2O_4--]_m}$  for double the bromide concentration. It is seen that these ratios range from

TABLE XI.—BROMIDE	RETARDATIONS	IN THE	C <sub>2</sub> O ,	REACTION.
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Bromide →	$M/2 \Rightarrow M/4$ .	$M/4 \rightarrow M/8$ .	$M/8 \rightarrow M/16$ .
λ = 546 μμ $λ = 436 μμ$ $λ = 365 μμ$	1.00 (1.02) 1.13 (1.14) 1.52 (1.12)	1.30 (1.53)	

1.0 to 1.45, that for constant  $\lambda$  they increase with decreasing [Br-], and for constant bromide concentration they increase with decreasing  $\lambda$ . The bracketed figures are calculated values (see page 378).

( $\beta$ ) The  $HC_2O_4^-$  Reaction.—Tables IX. and X. show that, owing to the higher intrinsic rate of the  $C_2O_4^-$  reaction, the  $HC_2O_4^-$  reaction has in no case been completely isolated. In the experiments with oxalic acid solutions (Table X.), however, the  $HC_2O_4^-$  reaction contributes the greater part of the observed effect, and it is possible, by correcting for the simultaneously occurring  $C_2O_4^-$  reaction, to arrive at the bromide retardation of the "pure  $HC_2O_4^-$  reaction." The details of this correction need not here be reproduced; the final results are to be found in

Table XII., which gives the bromide retardations of the HC<sub>2</sub>O<sub>4</sub><sup>-</sup> reaction at II·5°.

Bromide →	$M/4 \rightarrow M/8$ .	$M/8 \rightarrow M/16$ .	$M/16 \rightarrow M/32$ .	$M/32 \rightarrow M/64$ .
$\lambda = 546 \mu\mu$ $\lambda = 436 \mu\mu$ $\lambda = 365 \mu\mu$	5.10 (1.88) 5.09 (1.88)	1.81 (1.80) 1.88 (1.84)	1.48 (1.21) 1.48 (1.20) 1.48 (1.80)	1.47 (1.47) 1.40 (1.60) 1.87 (1.81)

TABLE XII.—Bromide Retardations in the HC2O4 Reaction.

Comparing Table XII. with Table XI., it will be seen that the retardation of the  $HC_2O_4^-$  reaction by bromide is considerably greater than that of the  $C_2O_4^-$  reaction. Another difference between the two reactions is that for the  $HC_2O_4^-$  reaction the bromide retardations increase with increasing [Br-], while Table XI. shows the reverse to be true for the  $C_2O_4^-$  reaction. The two reactions, however, possess one feature in common in that in both there is a definite increase in the bromide retardation with decreasing  $\lambda$ .

 $(\gamma)$  Mathematical Representation of the Bromide Retardations of the Two Reactions.—Of the two, the  $HC_2O_4^-$  reaction is the simpler, since it is found that its retardation by bromide may be quantitatively expressed by the equation

$$\gamma\sqrt{E} \propto \frac{\mathrm{I}}{\sqrt{[\mathrm{Br}^-]}} \times \frac{\mathrm{I}}{\sqrt{[\mathrm{Br}^-] + K_3 \frac{\alpha_1}{\alpha_2}}}$$
 (3)

in which the second term on the right-hand side is the one already used (p. 377) to account for the dependence of  $\frac{(\gamma\sqrt{E})_{\lambda_1}}{(\gamma\sqrt{E})_{\lambda_2}}$  on the bromide concentration. In Table XII, the comparison is made between the experimental retardations and those predicted by this equation (figures in brackets). It will be seen that over the range of KBr from M/8 to M/64 the agreement is satisfactory. The deviations which occur in the range  $[Br^-] = M/4 - M/8$  are to be attributed to the relatively large corrections which have to be applied in this region for the simultaneously occurring  $C_2O_4^-$  reaction, which make the experimental ratios considerably less accurate.

The effect of Br on the  $C_2O_4$  reaction is more complex, as evidenced by the fact that in contrast with both the  $HC_2O_4$  photo-reaction and the thermal reaction <sup>7</sup> the retardation now decreases with increasing [Br]. Since, however, it has been shown that for the  $C_2O_4$  reaction as for the  $HC_2O_4$  reaction, the expression for the rate (i.e., for  $\gamma\sqrt{E}$ )

contains the term 
$$\frac{1}{\sqrt{[Br^-] + K_3 \frac{\alpha_1}{\alpha_2}}}$$
, and since also the retardation is

now considerably less, it follows that the observed retardation can best be reproduced by an equation in which we have an additional term containing [Br-] in the numerator. Actually an equation of the type

$$\gamma\sqrt{E} \propto \frac{1 + K[Br^-]}{\sqrt{[Br^-]} \times \sqrt{[Br^-] + K_3 \frac{\alpha_1}{\alpha_2}}} \cdot \cdot \cdot (4)$$

is found to fit the results, K having a value 9.0 independent of the wavelength. In Table XI. the comparison is made between the observed bromide retardations and those calculated (bracketed values) on the basis of this equation.

#### (F) Temperature Coefficients.

The effect of temperature on the two reactions has been studied using light of wavelengths 365, 436 and 546  $\mu\mu$  at the four temperatures 6.5°, 11.5°, 16.5° and 21.5°. For the  $HC_2O_4^-$  reaction the following values of the ratio  $(\gamma\sqrt{E})_{\theta+5}/(\gamma\sqrt{E})_{\theta}$  were obtained: 1.52, 1.50, 1.51, 1.49, 1.47, 1.43, 1.42, 1.40 and 1.43, the figure being independent of the wavelength and of the bromide concentration. Taking the mean as 1.47, this corresponds to a temperature coefficient of (1.47)² or 2.16. For the  $C_2O_4^-$  reaction, the mean of nine determinations for a five degree rise was 1.44, and again the figure is independent of the wavelength and also of the Br- concentration. This corresponds to a temperature coefficient of (1.44)² or 2.07, in good agreement with Berthoud and Bellenot's value of 2.04 in white light. The  $HC_2O_4^-$  reaction thus appears to have a very slightly higher temperature coefficient than that of the  $C_2O_4^-$  reaction.

#### (G) The Effect of Addition of Ammonium Salts.

In their study of the photo-reaction between neutral oxalates and bromine, Berthoud and Bellenot found that addition of small quantities of ammonium salts caused induction periods. We have carried out a few experiments to test this observation, and have found that, while in the case of neutral oxalate NH<sub>4</sub> salts retard the reaction, they exert no appreciable effect on the HC<sub>2</sub>O<sub>4</sub>- reaction. Thus for a reaction mixture M/8 H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + M/32 KBr + M/600 Br<sub>2</sub> at 11·5° with  $\lambda$  = 546  $\mu\mu$ , we found  $\gamma\sqrt{E}$ . 10 - 7 = 6·5, while with the same reaction mixture plus M/1000 NH<sub>4</sub>NO<sub>3</sub> under the same conditions,  $\gamma\sqrt{E}$ . 10 - 7 = 6·6. With M/100 K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + M/4 KBr + M/600 Br<sub>2</sub>, however, at 6·5° and  $\lambda$  = 436  $\mu\mu$ , the figures in the absence and in the presence of M/5000 NH<sub>4</sub>NO<sub>3</sub> were  $\frac{\gamma\sqrt{E}}{[C_2O_4^{--}]_m}$ . 10 - 10 = 1·96 and 1·44 respectively.

Blank experiments showed that in the case of the last of these experiments (neutral oxalate reaction in the presence of  $\mathrm{NH_4}$  salt) about 50 per cent. of the ammonium salt had been thermally oxidised before the initial sample of the reaction mixture had been removed. It is probable that the bulk of the remainder was oxidised during the period of exposure. In spite of this, however, a fall in net quantum yield (calculated with respect to disappearance of  $\mathrm{Br_2}$ ) occurred, suggesting a considerable fall in the quantum yield of the  $\mathrm{C_2O_4}^{--}$  photo-oxidation process. The thermal oxidation of ammonium salts by bromine is a reaction very strongly retarded by H +, and consequently the complication of a simultaneous thermal reaction does not arise in the experiments with oxalic acid +  $\mathrm{Br_2}$  + ammonium salt, that is, with a solution of sufficiently high [H +]. It appears that the entity which causes the induction period is the  $\mathrm{NH_3}$  molecule formed by hydrolysis of the ammonium salt, and that the phenomenon only occurs at  $p_{\mathrm{H}}$  values greater than about 5.

#### II. THE PHOTO-REACTION OF IODINE WITH NEUTRAL OXALATE.

As this photo-reaction has already been the object of much intensive work 1, 2 which has succeeded in resolving its main features, we have

confined ourselves to one point only, viz, the nature of the function expressing the retardation by iodide ions. It may be stated at once that the function which our experimental observations suggest in the case of the  $I_2 - C_2O_4^{-}$  reaction is exactly analogous to that which we have shown to hold in the case of the photo-reaction between bromine and the acid-oxalate ion, where the retardation by bromide is expressed by

$$\gamma\sqrt{E} = \frac{const.}{\sqrt{[Br^{-}]\left\{[Br^{-}] + K_{3}\frac{\alpha_{1}}{\alpha_{2}}\right\}}} \quad . \tag{5}$$

In the latter case, since  $K_3$  is about 0.05 and  $\alpha_1$  and  $\alpha_2$  are of the same order of magnitude for wavelengths in the visible,  $\gamma\sqrt{E}$  becomes inversely proportional to [Br-] only for high values of [Br-], and considerable deviations from inverse proportionality to [Br-] can occur within the concentration range M/2 to M/50 of bromide.

For the iodine-oxalate reaction, although in the visible  $\alpha_1$  and  $\alpha_2$  are again of the same order of magnitude,  $K_3$  is considerably less, viz, 0.00138 at 25°. Even if the iodine-oxalate reaction obeys an equation analogous to (5), no deviations from inverse proportionality to [I<sup>-</sup>] would be detected in the range of iodide concentration above M/50. In agreement with this, Berthoud and Bellenot have shown that the rate of reaction is inversely proportional to [I<sup>-</sup>] in the range M/20-M/40, but did not extend their measurements to lower iodide concentrations. It is for this reason that we have reinvestigated the iodide retardation of this photo-reaction over a range of [I<sup>-</sup>] from M/100 to

M/1600 within which the term  $K_3 \frac{\alpha_1}{\alpha_2}$  becomes comparable with [I-].

The results definitely show that at low iodide concentrations the rate is not inversely proportional to  $[I^-]$ , but is proportional to  $\frac{I}{\sqrt{[I^-]\{[I^-]+Z\}}}$ ,

where Z is of the order of magnitude of  $K_3\frac{\alpha_1}{\alpha_2}$ . Experimental difficulties have prevented as complete a study of the iodine reaction as has been made of the bromine reaction. Thus, the necessity of having to restrict the measurements to regions of partial absorption of the incident light has limited us to the three wavelengths 436, 546 and 579  $\mu\mu$ . Further, for solutions weak in iodide, it was necessary to cut down as far as possible the increase in [I-] which occurs during insolation, in order that the mean value of [I-] should be of significance. It is only possible to do this by working with very low iodine concentrations, which naturally reduces the accuracy of measurement. Even so, considerable increases of [I-] occurred during the experiments, which were all carried out at 25° with solutions containing initially M/10 Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, with KI concentrations from M/100 to M/1600, and with iodine concentrations from M/1500 to M/3000.

Table XIII. contains a summary and analysis of the experimental data. From the initial concentrations of KI and iodine and the measured extent of the photo-reaction (Columns 1, 2 and 3), values of  $[I^-]_{\text{initial}}$  and  $[I^-]_{\text{final}}$  have been calculated. The  $[I^-]_m$  of Column 4 is the mean of these figures. The fifth column gives the values of  $\gamma\sqrt{E}$ , while the last three columns give the values of  $\gamma\sqrt{E}$  multiplied by three possible

iodide functions, 
$$viz.$$
,  $[I^-]_m$ ,  $\sqrt{[I^-]_m \left\{ [I^-]_m + K_3 \frac{\alpha_1}{\alpha_2} \right\}}$  and  $\sqrt{[I^-]_m}$  re-

spectively. The extinction coefficients  $\alpha_1$  and  $\alpha_2$  of  $I_2$  and  $I_3$  employed were  $\alpha_1 = 580$ , 131 and 63, and  $\alpha_2 = 1300$ , 134 and 70 at 436, 546 and 579  $\mu\mu$  respectively. The values at 546  $\mu\mu$  are those of Allmand and Young.<sup>2</sup> That of  $\alpha_2$  at 436  $\mu\mu$  is given by Winther, <sup>10</sup> while the remaining values were obtained by us by the thermopile-galvanometer method.

TABLE XIII .- IODINE-OXALATE REACTION.

Initial Concentrations.					13*	$K_3 \frac{\alpha_1}{\alpha_2}$ .	9.
[KI].	$\Sigma[1_2] \times 10^4$ .	4.104.	[[]], 103.	$\gamma \cdot \sqrt{E}$ .10 $^{-8}$ .	$\gamma \sqrt{E} \cdot [1^-]_m \cdot 10^{-5}$ .	$\times \sqrt{\frac{\gamma \sqrt{E \cdot 10^{-5}}}{[1^{-}]_m \left\{ [1^{-}]_m + K \right\}}}$	$\gamma \sqrt{E} \cdot \sqrt{[1-]}_m \cdot 10^{-6}$
		$\lambda = 43$	36μμ; K <sub>3</sub>	$\alpha_1/\alpha_2=0$	о•оообі.		
1/1600 1/800 1/400	3°57 3°92 3°97	2°04 2°18 2°29	0°742 1°33 2°55	1*18 0*72 0*41	0.87 0.96 1.06	1.12	3.51 5.63 5.08
					control	ean 1.17	
		$\lambda = 5$	<sub>4</sub> 6μμ; К <sub>3</sub>		0.0014.		
1/1600 1/800 1/400 1/200 1/100	3.68 7.09 7.30 7.32 7.60	2·03 4·78 4·42 3·78 2·82	0.742 1.56 2.62 4.95 9.74	0.880 0.556 0.340 0.204 0.108	0.62 0.43 0.83 1.01 1.02	1.12 1.13 1.10 1.14 1.12	2.41 2.17 1.74 1.44 1.06
					Ments	ean 1.12	
		$\lambda = 5$	79μ $\mu$ ; $K_3$	$\alpha_1/\alpha_2=0$	0.00125.		
1/1600 1/800 1/400	4*36 8*32 8*60	1.99 3.97 4.09	0.725 1.295 2.245	0.36 0.36	0.45 0.45 0.65 0.65	1.11	2.32 2.12 1.80
					M	ean 1.08	

Comparison of the last three columns shows that

$$\gamma\sqrt{E}\times\sqrt{[\mathrm{I}^{-}]_{m}\Big\{[\mathrm{I}^{-}]_{m}+K_{3}\frac{lpha_{1}}{lpha_{2}}\Big\}}=constant$$

best fits the experimental results. There appears little doubt therefore that for all iodide concentrations less than M/20 (the highest used by Berthoud and Bellenot) the halide retardation is of the same character for the  $I_2 - C_2O_4^{--}$  reaction as we have found for the  $Br_2 - HC_2O_4^{--}$ reaction.11

equation analogous to (4), viz. 
$$\gamma \sqrt{E} \propto \frac{I + K[I-]}{\sqrt{[I-]\left\{[I-] + K_3 \frac{\alpha_1}{\alpha_2}\right\}}}$$
, the constant  $K$ 

in the numerator being such that K[I-] is negligible compared with unity for [1-] < M/20.

Winther, Z. physikal. Chem., 108, 236, 1924.
 There remains the possibility that at higher iodide concentrations the functional dependence of rate upon [I-] might require to be expressed by an

Two further points call for comment. The first is that there appears to be a real difference between the intrinsic rates of the photo-reactions of iodine with  $K_2C_2O_4$  and with  $Na_2C_2O_4$ . With M/10 solutions of these oxalates, the value of  $\gamma\sqrt{E}$  (or the rate of reaction) with  $\lambda=546~\mu\mu$  and  $t=25^\circ$  is 12 per cent. greater for the potassium salt than for the sodium salt. The second point is that in a reaction mixture containing  $M/10~NaHC_2O_4+M/800~KI+M/1500~I_2$ , the observed rate is almost but not quite accounted for as a  $I_2-C_2O_4-$  reaction, in spite of the fact that in the solution used the ratio  $\frac{[C_2O_4-]}{[HC_2O_4-]}$  is only 1/20. Attributing the residual reaction to photo oxidation of  $HC_2O_4-$  ions by iodine, it is inferred that the intrinsic rate of the latter reaction in the above mixture is only about 1/70 of that of the  $I_2-C_2O_4-$  reaction.

#### Summary.

The photochemical reactions of bromine with neutral oxalate and with oxalic acid have been studied at 6.5°, II.5° and I6.5° with light of wavelengths between 579  $\mu\mu$  and 313  $\mu\mu$ .

(a) A convenient measure of the reactivity of any mixture is given by the function  $\gamma\sqrt{E}$ , where  $\gamma$  is the quantum yield and E is the rate of absorption of radiant energy (quanta per c.c. of beam per minute). Within an absorption range up to 85 per cent.,  $\gamma\sqrt{E}$  is found to be independent of (i) the initial concentration of bromine, (ii) the extent of reaction, (iii) the incident energy, and (iv) the dimensions of the reaction cell. For absorptions greater than 85 per cent.,  $\gamma\sqrt{E}$  progressively falls; the variation of this function with percentage absorption can be quantitatively accounted for on the basis of a reaction mechanism involving a bromine atom chain.

(b) Two independent processes occur, the one involving  $C_2O_4$  – ions, the other  $HC_2O_4$  – ions. These two processes are differently retarded by Br-ions; thus, with M/4 KBr the intrinsic rate of the  $C_2O_4$  – reaction is 100 times that of the  $HC_2O_4$  – reaction, while in the presence of M/32 KBr the ratio of the intrinsic velocities is 34, i.e., the  $C_2O_4$  – reaction is less strongly retarded by bromide. For both reactions the retarding influence of the Br-ion increases with decreasing wavelength.

(c) The temperature coefficient of the C<sub>2</sub>O<sub>4</sub> - reaction is 2.07, that of the

HC<sub>2</sub>O<sub>4</sub>- reaction 2·16.

(d) The results of all experiments are quantitatively reproduced by the equations:

$$\begin{split} &\text{for the HC}_2 \mathcal{O}_4 \text{- reaction}: \ \gamma \sqrt{E} = constant \ . \ \frac{[\text{HC}_2 \mathcal{O}_4 \text{--}]}{\sqrt{[\text{Br}^-] \Big\{ [\text{Br}^-] + K_3 \frac{\alpha_1}{\alpha_2} \Big\}}}, \\ &\text{for the C}_2 \mathcal{O}_4 \text{-- reaction}: \ \gamma \sqrt{E} = constant \ . \ \frac{[\mathcal{C}_2 \mathcal{O}_4 \text{---}] \{ \mathbf{I} + K[\text{Br}^-] \}}{\sqrt{[\text{Br}^-] \Big\{ [\text{Br}^-] + K_3 \frac{\alpha_1}{\alpha_2} \Big\}}}, \end{split}$$

where  $\alpha_1$  and  $\alpha_2$  are the extinction coefficients of Br<sub>2</sub> and Br<sub>3</sub>- respectively,  $K_3 = \frac{[\text{Br}_2][\text{Br}_3]}{[\text{Br}_3-]}$ , K is a constant whose value is 9.0, and the *constants* are functions only of wavelength and temperature.

The photochemical reaction of iodine with neutral oxalate has been studied at 25° with light of the three wavelengths 579  $\mu\mu$ , 546  $\mu\mu$  and 436  $\mu\mu$  in the presence of low concentrations of KI.

(a) The reaction conforms to the kinetic equation

$$\gamma \sqrt{E} = constant \cdot \frac{[C_2 O_4 - ]}{\sqrt{[I -] \left\{ [I -] + K_3 \frac{\alpha_1}{\alpha_2} \right\}}}$$

(b) The rate of reaction is somewhat greater with  $K_2C_2O_4$  than with  $Na_2C_2O_4$ .

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# THE PHOTO-REACTIONS OF OXALATES WITH BROMINE AND WITH IODINE. PART II—THEORETICAL.

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In the preceding paper (page 369) it has been shown that the photoreactions of oxalates with bromine and iodine in aqueous solution conform to the equations:

(a) for the Br<sub>2</sub> - HC<sub>2</sub>O<sub>4</sub> reaction :-

$$\gamma \sqrt{\bar{E}} = constant \cdot \frac{[\mathrm{HC_2O_4}^-]}{\sqrt{[\mathrm{Br}^-] \left\{ [\mathrm{Br}^-] + K_2 \frac{\alpha_1}{\alpha_2} \right\}}};$$

(b) for the  $Br_2 - C_2O_4^{-}$  reaction:—

$$\gamma \sqrt{E} = constant \cdot \frac{\left[C_2 O_4^{--}\right] \left\{1 + K[Br^-]\right\}}{\sqrt{[Br^-]\left\{[Br^-] + K_3 \frac{\alpha_1}{\alpha_2}\right\}}};$$

(c) for the  $I_2 - C_2O_4$  - reaction :—

$$\gamma \sqrt{E} = constant \cdot \frac{[C_2 O_4^{--}]}{\sqrt{[I^-]\{[I^-] + K_3 \frac{\alpha_1}{\alpha_2}\}}}.$$

In these equations,  $\gamma$  represents quantum yield, E is the rate of absorption of energy in quanta per c.c. of beam per minute,  $K_3$  is the equilibrium constant of trihalide formation,  $\alpha_1$  and  $\alpha_2$  are the molecular extinction coefficients of free halogen and trihalide ion respectively, and K is an (empirical) constant.

To interpret these expressions, it seems clear that, in agreement with previous investigators, we must postulate chain mechanisms in each

case with halogen atoms as carriers of the chain. After examination of a number of possibilities, it has been found possible to derive the above kinetic equations only on the basis of the two following mechanisms, both of which are modifications of the original mechanism of Berthoud and Bellenot.<sup>1</sup>

Mechanism 2 is identical, except for the introduction of the internal filter action, with the mechanism of Dickinson and Ravitz <sup>2</sup> for the  $I_2-C_2O_4^{--}$  reaction. It will be seen that the two mechanisms here suggested have different primary processes and different chain-breaking reactions, but have the same chain reactions (5)—(9), which are essentially those of Berthoud and Bellenot. Further, in both mechanisms the existence of the complex ion  $X_2^-$  is postulated. The necessity for this hypothesis is discussed later; for the present it suffices to state that reactions (4) and (4') are assumed to be rapid, so that throughout an experiment, the equilibrium defined by  $K_4 = \frac{k_4'}{k_4} = \frac{[X][X^-]}{[X_2^-]}$  is continuously maintained.

We first consider Mechanism I, in which the photochemically effective absorption is ascribed only to the halogen molecule while the trihalide ion is presumed to act as an internal filter. We shall deal only with the case of weak absorption from a beam whose cross section is equal to that of the cell. Under these conditions, let E= total rate of absorption of radiant energy in quanta per c.c. per minute,  $E_1=$  rate of absorption by the halogen and  $E_2=$  that by the trihalide ion. Then the rate of formation of X atoms by (I) = 2  $k_1E_1$ , where  $k_1$  is an efficiency factor for process (I). Postulating, for conditions of constant illumination, the attainment of "stationary" concentrations of X and  $X_2^-$ , we obtain (with all concentrations expressed in the units molecules/c.c.):

and, adding

$$k_1 E_1 = k_{10}[X_2^-][X]$$
 . . (15)

If now, we write 3

$$[X_2^-] = \frac{[X][X^-]}{K_4}$$

<sup>&</sup>lt;sup>1</sup> Berthoud and Bellenot, J. Chim. physique, 21, 308, 1924; Helv. Chem. Acta 7, 307, 1924.

<sup>&</sup>lt;sup>2</sup> Dickinson and Ravitz, J. Amer. Chem. Soc., 52, 4770, 1930.

<sup>3</sup> It is seen from equation (14) that this cannot be exactly true. The additional assumption is therefore necessary that the reciprocal processes (4) and (4') are rapid, compared with reactions (5)—(11).

we obtain from (15)

$$[X] = \sqrt{\frac{k_1 K_4 E_1}{k_{10}[X^-]}} \quad . \qquad . \qquad . \qquad (16)$$

For the absorption of a solution containing the two absorbing species  $X_2$  and  $X_3$ , we have

$$E_1 = E_{\frac{\alpha_1[X_2]}{\alpha_1[X_2] + \alpha_2[X_3^-]}},$$

where  $\alpha_1$  and  $\alpha_2$  are the molecular extinction coefficients of  $X_2$  and  $X_3^-$  respectively.

Further

$$[\mathbf{X_2}] = \frac{K_3}{K_3 + [\mathbf{X}^-]} \mathcal{E}[\mathbf{X_2}] \quad \text{and} \quad [\mathbf{X_3}^-] = \frac{[\mathbf{X}^-]}{K_3 + [\mathbf{X}^-]} \mathcal{E}[\mathbf{X_2}]$$

where  $\Sigma[X_2]$  is the concentration of titratable halogen and  $K_3 = \frac{[X^-][X_2]}{[X_3^-]}$ .

Thus,

$$E_{1} = \frac{K_{3} \frac{\alpha_{1}}{\alpha_{2}}}{[X^{-}] + K_{3} \frac{\alpha_{1}}{\alpha_{2}}} \cdot E \qquad . \qquad . \qquad (17)$$

Substitution in (16) gives

[X] = 
$$\sqrt{\frac{k_1 K_4 K_3 \alpha_1 E}{k_{10} \alpha_2 [X^-] \{ [X^-] + K_3 \frac{\alpha_1}{\alpha_2} \}}}$$
 (18)

From (18) the experimentally observed kinetic expressions are easily obtained.

(a) For the  ${\rm Br_2-HC_2O_4^-}$  reaction, by assuming (5) as the rate-determining step, we find

$$\begin{split} -\frac{d\Sigma[\mathrm{Br}_2]}{dt} &= k_5[\mathrm{Br}][\mathrm{HC_2O_4}^-] \\ &= k_5[\mathrm{HC_2O_4}^-] \sqrt{\frac{k_1 K_4 K_3 \alpha_1 E}{k_{10} \alpha_2[\mathrm{Br}^-] \left\{[\mathrm{Br}^-] + K_3 \frac{\alpha_1}{\alpha_2}\right\}}, \end{split}$$

from which, by an easy transformation

$$\gamma \sqrt{E} = k_5 \sqrt{\frac{k_1 K_4 K_3 \alpha_1}{k_{10} \alpha_2}} \cdot \frac{[\text{HC}_2 \text{O}_4^-]}{\sqrt{[\text{Br}^-] \left\{ [\text{Br}^-] + K_3 \frac{\alpha_1}{\alpha_9} \right\}}} \quad . \quad (19)$$

(b) For the  $\mathrm{Br_2}$ — $[C_2\mathrm{O_4}^{-}]$ —reaction, by assuming that both Br and  $\mathrm{Br_2}$ —react with  $C_2\mathrm{O_4}^{-}$ —, *i.e.*, that both reactions (6) and (7) occur, we obtain

$$\gamma \sqrt{E} = k_6 \sqrt{\frac{k_1 K_4 K_3 \alpha_1}{k_{10} \alpha_2}} \cdot \frac{\left[C_2 O_4^{--}\right] \left\{1 + \frac{k_7}{k_6 K_4} \cdot [Br^{-}]\right\}}{\sqrt{\left[Br^{-}\right] \left\{[Br^{-}\right] + K_3 \frac{\alpha_1}{\alpha_2}\right\}}} \quad . \quad (20)$$

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(c) For the  $I_2-C_2O_4-$  reaction, by assuming reaction (6) alone as the rate-determining step, it follows that

$$\gamma \sqrt{E} = k_6 \sqrt{\frac{k_1 K_4 K_3 \alpha_1}{k_{10} \alpha_2}} \cdot \frac{[C_2 O_4^{--}]}{\sqrt{[I^-] \left\{ [I^-] + K_3 \frac{\alpha_1}{\alpha_2} \right\}}} \qquad . \quad (21)$$

Equations (19), (20) and (21) based on Mechanism 1 are all in formal agreement with experiment. On further examination, however, Mechanism 1 is found to be untenable. This follows from an examination of Table VII. of the preceding paper (p. 377), in which are given relative values of  $K_{\lambda}$  for the Br<sub>2</sub> — HC<sub>2</sub>O<sub>4</sub><sup>-</sup> and Br<sub>2</sub> — C<sub>2</sub>O<sub>4</sub><sup>--</sup> reactions,  $K_{\lambda}$  being defined by the equation

$$\gamma \sqrt{E} \propto \frac{K_{\lambda}}{\sqrt{[\mathrm{Br}^{-}] + K_{3} \frac{\alpha_{1}}{\alpha_{2}}}} \quad . \qquad . \qquad (22)$$

and including those parameters which are dependent on  $\lambda$ , but independent of the bromide concentration. Comparison of this equation with equations (19) and (20) shows that on the basis of Mechanism 1:

$$K_{\lambda} = \sqrt{\frac{\overline{k_1 \alpha_1}}{\alpha_2}}$$
.

In this comparison, it is assumed that no variation of  $k_5$ ,  $k_6$  or  $k_7$  with  $\lambda$  occurs, although there is a possibility that at frequencies greater than the convergence limit the excess kinetic energy of the halogen atoms immediately after the optical dissociation of the molecule might promote reactions (5)—(7), and so increase the respective velocity constants. No such effect has, however, been observed for a photo-reaction of bromine in the gaseous phase (cf. Jost 4), and its occurrence is certainly more improbable in the liquid state, where the chances of deactivation are so much greater. We thus obtain

$$k_1 = \frac{\alpha_2}{\alpha_1} \cdot K_{\lambda}^2 \qquad . \qquad . \qquad . \qquad (23)$$

From the data of Tables V., VI., VII. and VIII. of the preceding paper, we have calculated values of  $K_{\lambda}^2$  for the bromine reactions relative to  $K_{\lambda}^2$  for  $\lambda=579~\mu\mu$ . These together with values of  $k_1$  calculated therefrom by applying equation (23) are given in Table I.

#### TABLE I.

	1						
$\lambda \ (\mu \mu) \ . \ . \ . \ K_{\lambda}^2 \ ({ m relative}) \ . \ k_1 \ ({ m relative}) \ .$	579 1.0 1.0	546 1.19 1.94	436 2·10 15·5	405 2*10 33*6	3 <sup>6</sup> 5 2 <b>·</b> 57 84 <b>·</b> 4	313 2.83 2570	

Now  $k_1$  is the efficiency of the primary process of the photo-reaction, and although in general quantum yields of photo-processes (and possibly also the efficiencies of primary processes) tend to increase with diminishing wavelength, an increase of the order of magnitude of that given in Table I. has never been observed. This result is certainly sufficient justifica-

<sup>4</sup> Jost, Z. physikal. Chem., 134, 92, 1928.

tion for rejecting Mechanism I; further, the large rise in  $k_1$  between 365  $\mu\mu$  and 313  $\mu\mu$ , together with the general similarity in the plots of log  $k_1$  and of log  $\alpha_2$  against  $\lambda$  both emphasise that this large increase in  $k_1$  with diminishing  $\lambda$  is a direct result of the passive rôle ascribed to  $\text{Br}_3$ —ions in Mechanism I. Of the terms on the right-hand side of equation (23),  $K_{\lambda}^2$  alters little with decreasing  $\lambda$ ,  $\alpha_1$  increases comparatively slowly, but  $\alpha_2$  increases very rapidly. The large (and improbable) increase in  $k_1$  with decreasing  $\lambda$  naturally results.

We therefore revert to Mechanism 2, in which the rôles of  $X_3^-$  and  $X_2$  are reversed,  $X_2$  acting now as an internal filter, while  $X_3^-$  absorbs in a photochemically effective manner. The chain-breaking reaction is also changed and is now assumed to be

$$X_2^- + X_2^- \to X_3^- + X^-$$
 . . (11)

We need not deduce the kinetic equations which emerge, since the method of procedure has already been indicated. The resulting expressions are:

(a) For the  $Br_2 - HC_2O_4$  reaction, assuming (5), (8) and (9) as chain reactions:

$$\gamma \sqrt{E} = k_5 K_4 \sqrt{\frac{k_2}{k_{11}}} \cdot \frac{[HC_2O_4^{-}]}{\sqrt{[Br^{-}]\{[Br^{-}] + K_3 \frac{\alpha_1}{\alpha_2}\}}}$$
 (24)

(b) For the  $Br_2 - C_2O_4^{--}$  reaction, assuming (6), (7), (8) and (9) as chain reactions:

$$\gamma \sqrt{E} = k_6 K_4 \sqrt{\frac{k_2}{k_{11}}} \cdot \frac{\left[C_2 O_4^{--}\right] \left\{1 + \frac{k_7}{K_4 k_6} [Br^{-}]\right\}}{\sqrt{[Br^{-}] \left\{[Br^{-}] + K_3 \frac{\alpha_1}{\alpha_2}\right\}}} \qquad (25)$$

(c) For the  $I_2 - C_2O_4^{--}$  reaction, with (6), (8) and (9) as chain reactions:

$$\gamma \sqrt{E} = k_6 K_4 \sqrt{\frac{k_2}{k_{11}}} \cdot \frac{[C_2 O_4^{--}]}{\sqrt{[I^{-}] \{[I^{-}] + K_3 \frac{\alpha_1}{\alpha_2}\}}} \quad . \tag{26}$$

As before, these kinetic expressions are in agreement with the experimental observations.

Comparison of equation (22) with equations (24)—(26) shows that, on the basis of Mechanism 2.

$$k_2 = K_{\lambda}^2$$
.

Combining the data of the preceding paper (Tables V.-VIII. and XIII.) with this relation, we obtain the results given in Table II., showing the variation of the efficiency of the primary process  $(k_2)$  with  $\lambda$  for the bromine reactions and for the iodine reaction.

TABLE II.

	Bromine Reactions.					Iodi	ne React	ion.	
$\lambda \ k_2$	579 0*35	546 0.42	436 0.72	405 0.74	365 0*90	313	579 o•85	546 0*95	436 1.00

The figures given are in each case relative to the value of  $k_2$  at the lowest wavelength studied. Increases of the efficiency of the primary process of this order of magnitude are of general occurrence in photochemical reactions, and in this respect Mechanism 2 is completely satisfactory. If these values of  $k_2$  are plotted against frequency  $(\nu)$ , it is found that for both reactions  $k_2$  is tending towards a maximum with increasing  $\nu$ , and the maximum appears almost to be reached at the lowest wavelengths investigated. The maxima clearly correspond to efficiencies of unity, and hence the figures of Table II. may be taken as giving approximately the actual values of  $k_2$  at various wavelengths, if Mechanism 2 be accepted.

It may be surmised that, since the dissociation of  $X_2$  makes no detectable contribution to the observed quantum yield,  $k_1$  cannot exceed about one-tenth the value of  $k_2$  at wavelengths such that  $\alpha_1$  and  $\alpha_2$  are of the same order of magnitude. Thus it may be estimated that  $k_1$  (546  $\mu\mu$ ) for  $I_2$  is less than 0.09, and  $k_1$  (546  $\mu\mu$ ) for  $I_2$  is less than 0.04. For the ultra-violet wavelengths, however,  $\alpha_2$  is much greater than  $\alpha_1$ , with the result that practically the whole of the absorption is due to  $X_3$ —ions. Under these circumstances  $k_1$  could conceivably rise to a value comparable with  $k_2$  (i.e.,  $X_2$  molecules could absorb effectively) without the dissociation of  $X_2$  contributing appreciably to the observed effect.

As Mechanism 2 satisfactorily accounts for the kinetic equations to which these reactions conform and is also not unsatisfactory in its predictions regarding the dependence of quantum yield on wavelength, it will be tentatively adopted and subjected to further discussion. This mechanism postulates that for photo-reactions of bromine and iodine in aqueous solution, the absorption by free halogen molecules constitutes an internal filter action. This assumption is a novel one, and on a priori grounds would appear to have little to recommend it. Yet,

the introduction of the term  $\sqrt{\frac{1}{[\mathrm{Br}^-]+K_3\frac{\alpha_1}{\alpha_2}}}$  in the kinetic expression

for the bromine reactions accounts remarkably well for the variation of the function  $\frac{(\gamma\sqrt{E})_{\lambda_1}}{(\gamma\sqrt{E})_{\lambda_2}}$  with bromide concentration and for the variation other

of the bromide retardation with wavelength, and no formulation other than one involving an internal filter action can be found which will yield the same result. In the absence of other physical or chemical evidence definitely opposed to the view that absorption of visible light by  $I_2$  and  $Br_2$  molecules in aqueous solution does not lead to atom formation, the present work furnishes, we consider, reasonable grounds for advocating this view.

Further features of Mechanism 2 are the postulation of the existence of the ion  $X_2^-$  and the assumption that the chain-breaking reaction is  $X_2^- + X_2^- \to X_3^- + X^-$ . The first hypothesis has already been made by Wagner, 5 Dickinson and Ravitz, 2 and Allmand and Young. 6 In the present instance the further assumptions are necessary (i) that the equilibrium  $X^- + X \rightleftharpoons X_2^-$  is rapidly attained and maintained even in the presence of the acceptor molecules  $(HC_2O_4^-$  and  $C_2O_4^{--})$  which are rapidly destroying and re-forming X atoms, and (ii) that  $K_4 = \frac{[X][X^-]}{[X_2^-]}$ 

<sup>&</sup>lt;sup>5</sup> Wagner, Z. physikal. Chem., 113, 261, 1924.

<sup>6</sup> Allmand and Young, Trans. Faraday Soc., 27, 515, 1931.

is small (see later) so that over ordinary ranges of concentration of X-the  $\rm X_2^-$  ion is present in considerable excess over the X atom.

Considering the chain-breaking reaction, there are the three possi-

bilities, viz.,

If all three reactions occur simultaneously, then on the basis of Mechanism 2, we obtain on illumination a stationary concentration of X atoms given by the equation:

[X] = 
$$\sqrt{\frac{k_2 E[X^-]}{\left\{k_{12} + \frac{k_{10}[X^-]}{K_4} + \frac{k_{11}[X^-]^2}{K_4^2}\right\} \left\{[X^-] + K_3 \frac{\alpha_1}{\alpha_2}\right\}}}$$
 (27)

The rate being proportional to [X] for the  $I_2 - C_2O_4^-$  and  $Br_2 - HC_2O_4^-$  reactions, it is clear that to obtain the experimentally observed halide retardation, it is necessary to assume that the term  $\frac{k_{11}[X^-]^2}{K_d^2}$  is

considerably greater than either  $k_{12}$  or  $\frac{k_{10}[X^-]}{K_4}$ , both of which are to

be neglected in comparison. On a priori grounds,  $k_{11}$  would be expected to be smaller than  $k_{12}$ , since the latter will approximate to a collision number while reaction (II) will possess an energy of activation, even if this only corresponds to the energy which the ions must possess to overcome each other's electrostatic fields. It therefore becomes necessary, as already indicated, to introduce the further assumption that  $K_4$  is small, so that it is the large excess of  $X_2^-$  over X which is responsible for the preponderance of reaction (II). Some justification of this assumption is given later.

Inspection of equations (24)—(26) shows that, in explaining the fact that the Br<sub>2</sub>— C<sub>2</sub>O<sub>4</sub>— photo-reaction has a different halide retardation from the other wo photo-reactions, we assume that both Br and Br<sub>2</sub>—react with C<sub>2</sub>O<sub>4</sub>—, whereas only Br (and not Br<sub>2</sub>—) reacts with HC<sub>2</sub>O<sub>4</sub>—and only I (and not I<sub>2</sub>—) reacts with C<sub>2</sub>O<sub>4</sub>—. Comparison of equation (25) with equation (4) of the preceding paper (p. ), shows that this

leads to  $\frac{k_7}{k_6K_4} = 9.0$ . Since, however,  $K_4$  is very small, this means that  $k_7 \ll k_6$  or the intrinsic rate of the reaction of Br<sub>2</sub>- with C<sub>2</sub>O<sub>4</sub>-- must be considerably smaller than that of the reaction of Br with C<sub>2</sub>O<sub>4</sub>--.

For the bromine reactions it is not possible to make any quantitative estimates of the magnitudes of the constants  $k_5$ ,  $k_6$ ,  $k_7$ ,  $k_{11}$  and  $K_4$  appearing in equations (24) and (25), but for the  $I_2 - C_2O_4^{-}$  reaction this may be done by correlating the photochemical data with measurements of the thermal reaction between iodine and oxalates. The result of this correlation also lends additional support to the hypothesis of an equilibrium  $I^- + I \rightleftharpoons I_2^-$ . The thermal reaction has been studied by Griffith and McKeown, who found that it occurs by two independent processes, of which one is semi-molecular with respect to iodine. This part of the reaction was found to conform to the kinetic law:

$$\frac{dx}{dt} = k_{\frac{1}{2}} [C_2 O_4^{--}] \sqrt{\frac{\Sigma[I_2]}{K_3 + [I^-]}} . (28)$$

<sup>&</sup>lt;sup>7</sup> Griffith and McKeown, Trans. Faraday Soc., 28, 752, 1932.

in which  $k_1$  is the semi-molecular velocity constant and  $\Sigma[I_2]$  the concentration of titratable iodine. The result was interpreted in terms of the mechanism:

This mechanism yields the expression

$$\frac{dx}{dt} = k_6 [C_2 O_4^{--}] \sqrt{\frac{K_{12} K_3 \Sigma[\bar{I}_2]}{K_3 + [\bar{I}^-]}} . \tag{29}$$

in which  $K_{12} = \frac{[1]^2}{[1_2]}$  is the equilibrium constant of the thermal dissociation of iodine into atoms.

Although the rate-determining reaction (6) is assumed to be the same for the thermal and photo-reactions, there is a striking difference between the iodide retardations of the two processes. The photo-reaction is the more strongly retarded; thus equation (28) shows that at high iodide concentrations, the thermal rate is inversely proportional to  $\sqrt{[I^-]}$ , but from equation (26) it is seen that under the same conditions the photo-rate is inversely proportional to  $[I^-]$ . The explanation of this difference is as follows. In the interpretation of the photochemical reaction, the participation of the equilibrium  $I^- + I \rightleftharpoons I_2^-$ , together with the chain-breaking reaction:

$$I_2^- + I_2^- \rightarrow I_3^- + I^-$$
 . . . . (II)

has been postulated. It follows therefore that in a *non-illuminated* solution of iodine in KI, we have, in addition to the equilibria (12) and (3), the equilibria:

These additional balanced reactions cannot, however, affect the stationary concentration of iodine atoms in the thermal system, and, independent of their occurrence, equation (29) must apply for the rate of the thermal reaction. In the photo-reaction, however, the stationary concentration of iodine atoms is given by equation (27), and here, depending on whether (12), (10) or (11) is assumed to be the effective chain-breaking process, we will obtain (for high values of [I-]) a photo-rate independent of [I-], or inversely as  $\sqrt{[I-]}$ , or inversely as [I-]. The fact that the photo-rate is found to be inversely proportional to [I-] decides that (11) is the preponderating chain-breaking process. It therefore follows that under thermal conditions the processes  $I_3 - + I - \rightleftharpoons I_2 - + I_2$  and  $I_2 - \rightleftharpoons I - + I$  (and not  $I_2 \rightleftharpoons 2I$ ) are predominant in the maintainance of the stationary iodine atom concentration in a solution of iodine in KI.

The assumption that (II) constitutes the chain-breaking reaction under photochemical conditions, made above to account for the kinetic

 $<sup>^8</sup>$  We may here refer to two points of similarity between the thermal and photoprocesses. (a) In both cases the rate of reaction is about 12 per cent. higher for potassium oxalate than for sodium oxalate; and (b) from both the thermal and photochemical data it has been shown that the specific rate of reaction between iodine atoms and  $\rm HC_2O_4^-$  ions is more than fifty times slower than that between iodine atoms and  $\rm C_2O_4^-$  — ions.

behaviour of the reaction, receives independent support from a comparison of the observed rates of the thermal and photo-processes. Identifying the thermal semi-molecular constant  $k_{\frac{1}{2}}$  of equation (28) with  $k_6\sqrt{K_{12}K_3}$  of equation (29), Griffith and McKeown have estimated  $k_6$  to be about  $4.5 \times 10^6$  at  $45^\circ$ , the units being  $\frac{\text{litres}}{\text{moles.min.}}$ have also shown  $k_{\bf 6}$  to have a critical increment of about 18,000 cals. It follows that  $k_6$  at 25° in the units  $\frac{\text{c.c.}}{\text{molecules. min.}} = 1.27 \times 10^{-15}$ .

Substituting this value in the expression for  $\gamma\sqrt{E}$  which naturally derives from equation (27), and applying the data of Table XIII. of the preceding paper referring to  $\lambda = 436 \mu\mu$ , it follows, independent of any assumption regarding the particular chain-breaking reaction, that

$$\sqrt{\frac{k_2[I^-]^2}{k_{12} + \frac{k_{10}[I^-]}{K_4} + \frac{k_{11}[I^-]^2}{K_4^2}} = 9 \times 10^{20} \quad . \tag{30}$$

Assuming that for this wavelength the efficiency  $(k_2)$  of the primary process is unity, and considering an iodide concentration of M/100, i.e., 6.1018 ions per c.c., then

$$k_{12} + \frac{k_{10}[I^-]}{K_4} + \frac{k_{11}[I^-]^2}{K_4^2} = 4 \times 10^{-5}$$
 (31)

An estimate of the value of  $k_{12}$  can be obtained by assuming that every collision between iodine atoms is effective in forming an iodine molecule;  $k_{12}$  is thus equal to the collision number, viz.  $3 \times 10^{-9}$ . Adopting this as a maximum value of  $k_{12}$  it follows that this term can be neglected in comparison with the other terms of the left-hand side of equation (31). Presumably the second term is intermediate in value between the first and third, and hence, in agreement with the assumption necessary to account for the nature of the iodide function, the first and second terms of equation (31) can be neglected in comparison with  $\frac{k_{11}[I-]^2}{K_4^2}$ , and it can be stated that, for the photochemical reaction,  $I_0 - + I_0 - \rightarrow I_0 - + I_0$ is the dominant chain-breaking process.

Continuing, we can obtain a maximum value for  $K_4$  by assuming that the maximum value of  $k_{11}$  is equal to the collision number between two  $I_2$  ions. Thus, from equation (30) we have

$$K_4/\sqrt{k_{11}} = 9 \times 10^{20}$$
,

and taking  $k_{11}=5\times 10^{-9}$ , we obtain  $K_4$  (maximum) to be of the order  $6\times 10^{16}$  (molecules/c.c.) or  $10^{-4}$  (moles/litre). It follows that with an iodide concentration of M/100, the concentration of I2- ions is at least 100 times that of iodine atoms, and, since  $k_{11}$  is probably several powers of ten less than the collision number, the concentration of I2- would appear, in agreement with the original premise, to be very much in excess of the iodine atom concentration throughout the range of iodide concentration investigated. The mean iodine atom concentration during a particular experiment follows from equations (27) and (30) together with the pertinent values of  $[I^-]_m$  and E. Thus for the solution M/400 KI + $M/1500~{\rm I_2}$  illuminated with  $\lambda=546~\mu\mu$  (see preceding paper, Table XIII., sixth experiment), we have  $[I^-]_m=1.57\times 10^{18}$  ions per c.c., E=

 $4.49 \times 10^{16}$  quanta per c.c. per minute, and [I] =  $10^{11}$  atoms per c.c.

or  $2 \times 10^{-10}$  gm. atoms per litre.

Finally, it is possible to obtain an approximate estimate of the temperature coefficient of  $K_4$ . In equation (26) the temperature coefficient of  $\gamma \sqrt{E}$  for the visible wavelengths is given by the data of Berthoud and Bellenot <sup>1</sup> and of Allmand and Young <sup>6</sup> as 3·I between 25° and 35°. In the same range  $k_6$  has according to Griffith and McKeown <sup>7</sup> a tem-

perature coefficient of 2·42. Hence that of  $K_4\sqrt{\frac{k_2}{k_{11}}}$  is equal to 1·28. The temperature coefficient of  $k_2$  is doubtless unity and that of  $k_{11}$  cannot be very different. Hence this value of 1·28 refers almost entirely to  $K_4$ . This would correspond to a positive heat of formation of  $I_2$ —ions from I atoms and I—ions of 4500 cals.

#### Summary.

The experimental data of the preceding paper for the photo-reactions of bromine and iodine with oxalates have been interpreted in terms of reaction mechanisms which postulate that:

(a) The effective primary process is a photo-dissociation of the trihalide

ion, the free halogen acting as an internal light filter.

(b) The bulk of the halogen atoms (X) formed by the primary process are transformed into  $X_2$ —ions via the equilibrium  $X + X = X_2$ .

(c) The rate-determining reactions are:

$$\begin{array}{c} HC_2O_4^- + Br \rightarrow C_2O_4^- + H^+ + Br^- \\ C_2O_4^- - + Br \rightarrow C_2O_4^- + Br^- \\ C_2O_4^- - + Br_2^- \rightarrow C_2O_4^- + 2Br^- \\ C_2O_4^- - + I \rightarrow C_2O_4^- + I^- \end{array}$$

and

and these are followed by reactions of  $C_2O_4$ - with Br<sub>2</sub> (and Br<sub>3</sub>-) or I<sub>2</sub> (and I<sub>3</sub>-) with regeneration of Br or I atoms.

 $\left(d\right)$  In all cases the effective chain-breaking reaction is that represented by :

$$X_2^- + X_2^- \rightarrow X_3^- + X^-$$
.

The authors wish to record their thanks to the Department of Scientific and Industrial Research for a maintenance grant to one of them (A. G. W.).

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# THE INFLUENCE OF TRACES OF A SALT OF TIN IN ACID SOLUTION ON THE RATE OF CORROSION OF MILD STEEL.

By T. N. Morris, M.A. (Cantab) and J. M. Bryan, B.Sc. (Lond.).

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It is to be expected that a metallic impurity of high over-voltage would, if deposited on its surface, have an inhibiting action on the corrosion of iron by an acid. Watts 1 demonstrated such an effect for

<sup>1</sup> O. P. Watts, *Trans. Am. Electrochem. Soc.*, **21**, 337, 1912; also O. P. Watts and N. D. Whipple, *ibid.*, **32**, 257, 1917.

salts of arsenic and considered that the inhibition was due to a deposition of arsenic on the surface of the iron causing polarisation of hydrogen; Thiel and Keller<sup>2</sup> observed that when iron was immersed in solutions of a stannous salt, in which the concentration of acid was not excessive. deposition of metallic tin occurred which prevented further solution of the iron; and, finally, Kohman 3 showed that the mere presence of a strip of tin in the same vessel as a strip of steel, but without contact. was sufficient to cause a marked inhibition of the corrosion of steel by acid which could only be ascribed to the influence of small quantities of tin salts in solution.

The present paper deals (a) with the effect on the rate of corrosion of steel by a solution containing 5 gm. of citric acid per litre together

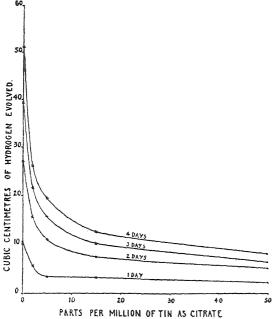


Fig. 1.—The effect of tin salts in solution on the progress of corrosion of steel, as shown by the production of hydrogen on successive days.

a varying amount of tin as tin citrate, and (b) with the effect of varying the hydrogen-ion concentration of the solution of citric acid by means of sodium citrate, the amount of tin in a given volume remaining constant (4 mg. per litre).

The apparatus used in following the corrosion has been described by Morris Bryan 4 and consists essentially of bottle of about 250 c.c. capacity containing the acid solutions and metal testpiece and held in a thermostat at 25° C. Any hydrogen produced is collected in gas burette attached to the bottle,

an arrangement which also gives a measure of the rapidity and extent of the corrosion.

In the first experiment the quantities of tin as citrate, added to separate units of the type just described, amounted to 2, 5, 15 and 50 parts per million, respectively, and controls containing no tin were also set up. Each unit was freed from air which was replaced by pure nitrogen and the progress of corrosion was followed by daily measurements of the hydrogen evolved (see curves of Fig. 1). The loss in weight

<sup>A. A. Thiele and K. Keller, Z. anorg. chem., 68, 220, 1910.
E. F. Kohman, "Factors affecting the Relative Potentials of Tin and Iron," Ind. and Eng. Chem., 20, 1373, 1928.
T. N. Morris and J. M. Bryan, "The Corrosion of the Tinplate Container by Food Products," D.S.I.R. Special Report of the Food Investigation Board, No. 40,</sup> p. 23.

of the test pieces (in duplicate) is shown in Table I. and graphically in Fig. 2.

TABLE I.—THE LOSS IN WEIGHT OF SPECIMENS OF STEEL IMMERSED IN A 0.5 PER CENT. SOLUTION OF CITRIC ACID CONTAINING VARYING AMOUNTS OF TIN AS CITRATE.

Parts per million of Tin.	0.	2.	5.	15.	50.
	o·1288 o·1158	o·o659 o·o578	0·0500 0·0491	0.0347 0.0310	0·0226 0·0201
Mean loss	0.1223	0.0618	0.0495	0.0328	0.0213

It can be seen that the addition of very small amounts of tin has a powerful inhibiting effect on corrosion, two parts per million being

sufficient to reduce the rate by nearly onehalf. Succeeding increments of tin do not exert a corresponding inhibition, a form of behaviour which seems to be characteristic of inhibitors, as was observed by Warner 5 who studied the inhibiting power of gelatin on the acid-corrosion of iron and by the authors 6 in work similar to the present on the effect of cane sugar.

In the second experiment illustrating the effect of hydrogenion-concentration on the efficiency of a given quantity of tin

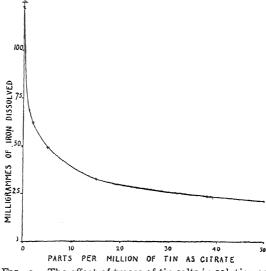


Fig. 2.—The effect of traces of tin salts in solution on the corrosion of steel.

(4 mg. per litre) in inhibiting corrosion, the solution of citric acid was buffered with sodium citrate over the range  $p_H$  2.4 to 5.5.

The apparatus was similar in all respects to that used previously, but, in this case, air was not excluded completely, there being about 12 c.c. in the headspaces of the bottles in addition to that in solution in the liquid.

In this respect, therefore, the results of the two experiments are not strictly comparable quantitatively, but the difference is not sufficient to affect seriously any question of principle.

In Fig. 3 three curves, A, B and C, are shown. A represents the normal

<sup>J. C. Warner, "Organic Type Inhibitors in the Acid Corrosion of Iron," Trans. Amer. Electrochem. Soc., 55, 287, 1929.
T. N. Morris and J. M. Bryan, loc. cit., p. 58.</sup> 

corrosion curve obtained over the  $p_{\rm H}$  range for a three-day period with no tin present in the solutions under the conditions of this experiment, C is the corresponding three-day curve with 4 parts per million of tin in each solution; B shows the curve obtained when the corrosionperiod is prolonged for seven days with 4 parts per million of tin

It will be seen that the curve C4 has a slight maximum at  $p_H$  3, but is, on the whole, fairly horizontal; it approaches the normal curve much more closely at low than at high acidity. In the seven-day curve, B, corrosion at the acid end has gained ground, but the general outline of the previous curve can still be traced.

The tendency for inhibitors to be relatively less efficient at low than

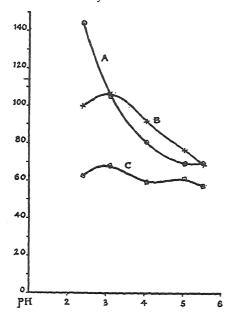


Fig. 3.—The effect of H-ion concentration on the efficiency of a salt of tin as an inhibitor of the corrosion of iron by citric acid.

at high acidity has been pointed out in a previous publication,7 being particularly striking in the case of gelatin. The reason for this is not certain but the work of Friend Vallance,8 and Chappell. Roetheli and McCarthy,9 Kuhn 10 Rhodes and others has made it fairly clear that the action of an inhibitor is to oppose a change in the physical state of the products of a chemical action and that, in the case of the corrosion of a metal by an acid, it raises the overvoltage and opposes the liberation of bubbles of The hydrogen. work of Bengough 11 indicates under certain conditions the hydrogen formed in corrosion passes directly into solution and may be given off from the surface of a liquid without appearing in bubble form, and the authors have repeatedly observed that large quantities

of hydrogen may be evolved by corrosion of iron in solutions of  $p_{\rm H} > 4$ without visible formation of bubbles.

It seems likely, therefore, that inhibitors act most efficiently where

<sup>7</sup> T. N. Morris and J. M. Bryan, loc. cit., p. 68; and T. N. Morris and J. M.

Bryan, Annual Report of the Food Investigation Board, 1930, p. 119.

<sup>8</sup> J. A. N. Friend and R. H. Vallance, "The Influence of Protective Colloids" on the Corrosion of Metals and on the Velocity of Chemical and Physical Changes,'

J. Chem. Soc., 121, 466, 1922.

<sup>9</sup> E. L. Chappel, B. E. Roetheli and B. Y. McCarthy, "The Electrochemical Action of Inhibitors on the Acid Solution of Iron and Steel," Ind. and Eng. Chem., **20,** 582, 1928.

10 F. H. Rhodes and W. E. Kuhn, "Inhibitors in the Action of Acid on Steel," Ind. and Eng. Chem., 21, 1066, 1929.
 G. D. Bengough, J. M. Stuart and A. R. Lee, Proc. Roy. Soc., 121A, 88,

1928.

there is active evolution of hydrogen as bubbles, and that they do not oppose, to the same extent, the type of corrosion in which the hydrogen passes directly into solution.

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#### THE INFLUENCE OF HIGH FREQUENCY CUR-RENTS POLARISED ELECTRODES. ON PART II.

By S. Glasstone and G. D. Reynolds.

Received 16th November, 1932.

The investigations described in the previous paper of this series (Part I.) indicated that high frequency currents are able to increase the rate of reaction between a depolariser and hydrogen at a polarised cathode. Although it appeared probable that the increased depolarisation was due to an increase in the rate of diffusion, the possibility of an increase in the velocity constant of the reaction was not excluded. Further, even if the change in the diffusion rate were the main cause of the H.F. effect, it had not been established whether this was due to an alteration in the diffusion constant or in the thickness of the diffusion layer. The present work was undertaken to determine, if possible, which of the three factors, viz., change in (a) velocity constant, (b) diffusion coefficient, or (c) diffusion layer, was the main cause of the depolarisation resulting from the application of high frequency currents.

In order to eliminate the possibility of an increase in the velocity constant being the origin of the H.F. effect, depolarisers were chosen which react very rapidly in comparison with the rate at which they diffuse to the electrode. The maximum rate of depolarisation is then governed entirely by the rate of diffusion of the oxidising agent to the cathode. Ferricyanide and ferric ions were shown to satisfy these conditions and were used in the preliminary work; subsequently other depolarisers, both anodic and cathodic, were employed in order to confirm the results obtained.

If the current passing through a cell containing a depolariser is gradually increased, a point is reached at which the rate of reduction of the depolariser at the cathode is equal to its maximum rate of diffusion in the electrolyte being used. Up to this point the cathode potential will remain in the vicinity of the reversible oxidation-reduction potential of the system, but any further increase in the polarising current will cause the electrode potential to become rapidly more negative until a value is reached at which another process, e.g., hydrogen evolution, becomes possible. The maximum current able to pass without causing gas evolution is here called the "limiting current" (for 100 per cent. reduction efficiency). The value of the limiting current may be calculated from the following equation, which can be deduced from Fick's Law:

 $i_0 = 1117 \, ADc/l \, \text{microamps.},$ 

<sup>&</sup>lt;sup>1</sup> Glasstone and Reynolds, Trans. Faraday Soc., 28, 582, 1932. <sup>2</sup> See Glasstone, Trans. Amer. Electrochem. Soc., 59, 277, 1931.

where  $i_0$  is the limiting current in microamps., D is the diffusion coefficient of the depolariser, expressed in g. equiv./sq. cm./day units, c is its concentration in g. equiv. per litre, A is the electrode area in sq. cm., and l is the thickness of the diffusion layer. It must be mentioned that in the deduction of this equation, in addition to presupposing a very rapid depolarising reaction, it is assumed that none of the depolariser is brought up to, or removed from, the vicinity of the cathode as a result of transport by the current; in the present experiments the concentration of depolariser was small in comparison with that of the other ions, so that nearly the whole of the current is carried by the latter and only a negligibly small amount by the depolariser.

From a number of observations involving different types of electrode reactions it has been found 3 that at ordinary temperatures, in an unstirred solution, the thickness of the diffusion layer (1) may be taken as 0.05 cm. The diffusion coefficients of ferric and ferricyanide ions are assumed to be I-O and I-3 respectively, the latter ion having an unusually large mobility.4 The values for the limiting current at a given electrode may thus be calculated for solutions of any particular concentration of depolariser by substitution in the equation given above. The observed limiting currents were found to be in close agreement with the calculated values, and hence it may be considered that with ferric and ferricyanide ions the rate of diffusion is the limiting factor in determining the maximum rate of reaction at the cathode. Experiments have now shown that even in the presence of such depolarisers the limiting current can be markedly increased by the application to the cathode of high frequency oscillations; these oscillations are, therefore, able to increase the rate of diffusion of the depolariser to the cathode. This paper describes observations of the H.F. effect on the limiting current in various solutions under a variety of conditions made with the object of throwing light on the mechanism of the effect.

#### Experimental.

The apparatus used was identical with that employed in the previous work.1 Before taking measurements a stream of nitrogen was passed through the electrolyte in the cell to remove any oxygen which would have acted as a depolariser in addition to the oxidising ions of known concentration; the gas current was stopped and the solution allowed time to come to rest before observations were made. In the preliminary experiments the polarising current was increased in steps and the cathode potential determined after each such increase; curves of the type shown in Fig. 1 were obtained with ferricyanide as depolariser, with 100 and 150 milliamps. and without applied high frequency oscillations. In later work the whole of the curve was not studied, but only its central portion; in each case the polarising current remained constant over a considerable range of potential, and this constant value was taken as the limiting current under the particular conditions employed. It must be stated that the values obtained for the limiting current are by no means exact, since various factors, some of which appear to be beyond the control of the observer, affect the results. In actual practice the measurements were repeated, without and with high frequency oscillations alternately, until the values were reasonably reproducible; on the whole it can only

Wilson and Youtz, J. Ind. Eng. Chem., 15, 603, 1923; Glasstone, loc. cit.
 Hölzl, Monatshefte, 55, 132; 56, 79, 1930.

be claimed, however, that the limiting currents reported are accurate to within 10 per cent. In view of the large relative magnitude of the H.F. effect this error is not serious.

The electrode used throughout the major portion of this work was of platinum wire having an exposed area of 6.5 sq. mm. and a diameter of 0.053 cm.; the results appear to be independent of the nature of the electrode material. Unless otherwise stated the experiments were carried out in unstirred solutions at room temperature (about 17°).

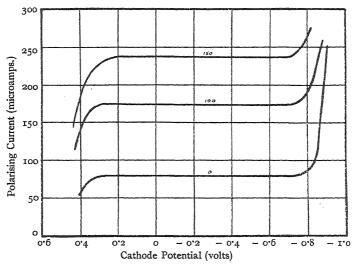


Fig. 1.—Influence of high frequency oscillations (100 and 150 milliamps.) on the limiting current.

#### Results.

**H.F.** Effect on the Limiting Current.—The observed and calculated values of the limiting current without high frequency oscillations  $(i_0)$  and the observed values under the influence of 150 milliamps. of high frequency current  $(i_h)$  for a number of solutions are given in Table I.

TABLE 1.—LIMITING CURRENTS IN MICROAMPS.							
i <sub>0</sub> (Calc.).	ι <sub>0</sub> (Obs.).	$i_h$ .	$i_h - i_0$ .				
Ferricyanide Depolariser in 0·1 N-NaOH.							
76	8o	240	160				
38	36	144	108				
19	18	74	56				
9.5	8	42	34				
ser in N-H <sub>2</sub> S	SO <sub>4</sub> .						
97	108	196	88				
48	50	105	55 38				
32	32	70					
24	22		34				
10	18	50	32				
	i <sub>0</sub> (Calc.).  polariser in 76 38 19 9.5  ser in N-H <sub>2</sub> S 97 48 32	$\begin{array}{ c c c c c c } \hline i_0 \text{ (Calc.).} & i_0 \text{ (Obs.).} \\ \hline polariser in 0.1 N-NaOl \\ 76 & 80 \\ 38 & 36 \\ 19 & 18 \\ 9.5 & 8 \\ \hline ser in N-H_2SO_4. \\ \hline 97 & 108 \\ 48 & 50 \\ 32 & 3^2 \\ 24 & 22 \\ \hline \end{array}$	$\begin{array}{ c c c c c c c c c } \hline i_0 \text{ (Calc.).} & i_0 \text{ (Obs.).} & i_h. \\ \hline polariser in 0 \cdot 1 & N-NaOH. \\ \hline 76 & 80 & 240 \\ 38 & 36 & 144 \\ 19 & 18 & 74 \\ 9 \cdot 5 & 8 & 42 \\ \hline ser in N-H_2SO_4. \\ \hline 97 & 108 & 196 \\ 48 & 50 & 105 \\ 32 & 32 & 70 \\ 24 & 22 & 56 \\ \hline \end{array}$				

TABLE I.-LIMITING CURRENTS IN MICROAMPS.

Considering the difficulty of obtaining exact values of the limiting current the agreement between the observed and calculated value of  $i_0$  is sufficiently good to justify the use of ferricyanide and ferric ions in the present work on the influence of high frequency oscillations. With both of these depolarisers there is no doubt, from the results quoted in Table I., that the oscillations cause a marked increase in the limiting current, and this can only be due to an increase in the rate of diffusion of the depolariser to the cathode.

It is known from the work of Debye and Falkenhagen, and of others. 5 that the mobility of an ion may be greater under the influence of high frequency currents than when low frequency or direct currents are used. Since the diffusion coefficient of an ion is related to its mobility under the influence of a fall of potential,6 it would not be surprising to find that high frequency currents brought about an increase in the diffusion coefficient of an ion. This explanation of the H.F. effect could not apply, however, to the experiments described in this paper; in the first place, the effects noted in the present work are much greater than those observed in connection with ionic mobilities, and in the second place the frequency of the oscillations used is only one-hundredth of the frequency which, according to the Debye theory, might be expected to show any effect at all. It is also significant that the rate of diffusion of a non-ionic depolariser, e.g., oxygen (see Part I.) or quinone (see below), can be increased by the application of high frequency alternations.

Influence of Frequency Variation.—As far as could be determined the influence of high frequency oscillations on the limiting current in the presence of depolarisers was found to be the same at all frequencies within the range of 0.1 to  $2 \times 10^6$  cycles per second. The high frequency E.M.F. required to pass a given current through the electrolytes used appeared also to be independent of the oscillation frequency. For the work described in this paper a constant frequency of  $10^6$  cycles per second was used.

Influence of High Frequency Current Strength.—The dependence of the H.F. effect on the strength of the limiting current was determined by measuring the limiting current  $(i_h)$  in a 0-02 M-ferricyanide solution in 0-1 N-sodium hydroxide at a series of increasing and decreasing values of high frequency current. The results for any one current are not in exact agreement although the divergencies do not amount to more than 10 per cent.; the figures are sufficiently definite, however, to indicate that the H.F. effect on the limiting current, for a given electrode and electrolyte, is directly proportional to the current strength. The observed values of  $i_h$ , in microamps., together with those calculated from the linear equation  $i_h - i_0 = 0.64 \ h$ , where h is the high frequency current strength in milliamps., and  $i_0$  is 38 microamps. (see Table I.), are given in Table II.

TABLE II.—H.F. EFFECT AND CURRENT STRENGTH.

$h$ $i_h$ (obs.) . $i_h$ (calc.) .	50 64-70 70	75 82-90 86	100 95-105 102	125 113-122 118	150 134-144 134	175 147-152 150	
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 <sup>&</sup>lt;sup>5</sup> Physikal. Z., 29, 1244, 1928; see Glasstone, "The Electrochemistry of Solutions," p. 135, 1930.
 <sup>6</sup> Nernst, Z. physikal. Chem., 2, 613, 1888.

Influence of Added Salts.—It has been shown in Part I.  $^{(1)}$  that the addition of salts to the electrolyte decreases the H.F. effect on potential probably as a result of the decrease in the high frequency resistance and E.M.F.; a similar diminution has been observed in the H.F. effect on the limiting current in the presence of depolarisers. The results in Table III. are for a 0.02 M-ferricyanide solution in 0.1 N-sodium hydroxide to which various amounts of salts were added; a high frequency current of 150 milliamps. Was used.

		Limiting	g Currents in M	icroamps.
Added Salt.		$i_0$	<i>i<sub>h</sub></i> .	$i_h - i_0$ .
M-NaCl		36 38 38 38 38 34 34	144 91 100 91 91 125	108 53 62 53 57 94

TABLE III.—ADDED SALTS AND THE H.F. EFFECT.

In every case the addition of an indifferent salt produces a definite decrease in the value of  $i_h$ , although  $i_0$ , as is to be expected, remains almost constant.

Influence of Physical Factors.—In an attempt to discover the cause of the increased rate of diffusion resulting from the application of high frequency currents, the influence of the viscosity and surface tension of the solution, of stirring and of raising the temperature on the H.F. effect on the limiting current was studied. Although the results are of interest they do not permit of a definite conclusion being reached as to which of the two factors able to increase the rate of diffusion of depolariser to the electrode, viz., increase of the diffusion coefficient or decrease of the diffusion layer, is responsible for the H.F. effect.

Viscosity.—The solutions used were 0.02 M-potassium ferricyanide in 0.1 N-sodium hydroxide containing in addition 10 (I), 20 (II) and 30 (III) per cent. by weight of ethyl alcohol, and a 0.022 M-ferric alum solution in N-sulphuric acid containing 5 (I), 12.5 (II) and 25 (III) per cent. by weight of glycerol; the viscosity of each solution relative to that of the depolariser solution containing no added substance was measured by means of an Ostwald viscometer. The limiting currents in these solutions, with and without high frequency oscillations, were determined; observations were made at the same time on the ordinary depolariser solution for purposes of comparison. The results of this work are given in Table IV.; with the ferricyanide depolariser the values of  $i_h$  refer to 125 milliamps. and for the ferric depolariser to 150 milliamps. of high frequency current. The relative viscosity is represented by the symbol  $\eta$ .

It is reasonable to assume that the diffusion coefficients of the depolariser ions will be inversely proportional to the viscosities of the solutions, and so it follows that for a given depolariser at a given concentration the product of the relative viscosity and the limiting current  $(i_0)$  should be constant, provided the thickness of the diffusion layer does not alter.

Comparison

Ι

 $\mathbf{II}$ 

III

1.00

1.15

1.38

1.01

30

25

24

Limiting Currents in Microamps. Solution.  $i_{0}n$ .  $i, \eta$ .  $i_h - i_0$ . Ferricyanide Depolariser. Comparison 126 36 126 90 1.00 36 23 32 142 1.39 102 79 T 84 34 38 210 II 2.10 16 100 III 100 270 2.70 Ferric Depolariser.

64 58

56

30

29

33

34

70

74 81

107

40

39

34 38

TABLE IV .- VISCOSITY AND THE H.F. EFFECT.

The values of  $i_0\eta$  in Table IV. are almost constant for each depolariser, and so it may be concluded that the thickness of the diffusion layer remains constant at 0.05 cm. If the high frequency oscillations increase the diffusion coefficient of the depolariser without affecting the diffusion layer, it might be anticipated that in the experiments under consideration the product of  $i_h\eta$  should be constant for each depolariser, at a constant value of high frequency current. This is certainly not the case, and so it appears at first sight that a change in the diffusion coefficient cannot be the cause of the H.F. effect on the limiting current. This argument is not rigid, however, since the H.F. effect, if any, on the diffusion coefficient might not be the same in each solution of a series.

Surface Tension.—The measurements made with the ferricyanide solutions to which alcohol was added (Table IV.) appeared to establish the fact that the H.F. effect was independent of the surface tension of the electrolyte (see last column), but as the change of viscosity introduced an added complication some experiments were made with 0.02 M-ferricyanide containing about 1.5 per cent. by weight of iso-amyl The surface tension of this solution was 33 dynes per cm., and the values of  $i_0$  and  $i_h$ , for 150 milliamps. of high frequency current, were 36 and 134 microamps. respectively. These residual currents fare in good agreement with the corresponding values of 36 and 144 or the ordinary aqueous electrolyte, having a surface tension of about 7<sup>3</sup> dynes per cm. There is no clear evidence, therefore, that a change in the surface tension alters either the diffusion layer, or the effect on it of high frequency oscillations.

**Influence of Stirring.**—By stirring an electrolyte vigorously it is possible to reduce the thickness of the diffusion layer to a tenth, or less, of its value in a still solution; the diffusion coefficients, however, remain unchanged. This change is the opposite of that resulting from an increase of viscosity of the electrolyte. The limiting currents, without and with 125 milliamps. applied high frequency current, were measured in the following solutions when still and also with the test electrode rotated at the rate of 500 r.p.m.: (I) 0.002 M-ferric alum in 0.04 N-sulphuric acid, and (II) 0.002 M-ferricyanide in 0.04 N-sodium hydroxide. The results obtained are given in Table V.

		Limiting Currents in Microamps.							
		Still.	Stirred.	Still.	Stirred.				
$i_0 \\ i_h \\ i_h/i_0$ .	•	9.1 3.1	28 36 1·3	3·5 20 5·7	39 48 1·2				

TABLE V.-Stirring and the H.F. Effect.

Similar results were obtained with a stationary electrode when the solution was stirred by the passage of a rapid stream of nitrogen. The figures in Table V. do not seem to be explicable on the basis of the view that high frequency currents increase the coefficient of diffusion, since it would be implied that this coefficient is different in stirred and unstirred solutions under the influence of high frequency oscillations. Such a difference might be explained by assuming that the H.F. effect on the diffusion coefficient is different according to whether the electrolyte is still or stirred, but this does not seem very probable. The results quoted in Table V. are not, however, in disagreement with the view that the high frequency currents decrease the thickness of the diffusion layer; since stirring decreases the thickness of this layer it is not unreasonable to suppose that the effect of any additional influence operating in the same direction will be relatively small.

Influence of Temperature.—Some observations have been made of the H.F. effect on the limiting current in a 0.022 M-ferric alum solution in N-sulphuric acid at a series of temperatures from 17° to 50°; as the temperature increases the results become less reproducible, as radiation from the surface of the solution causes stirring by convection currents. The approximate values for the limiting currents without and with 150 milliamps. of high frequency current are given in Table VI.

TABLE	VI.—TEMPERATURE	AND	THE	H.F.	Effect.

	Limiting Currents in Microamps.					
Temp.	$i_0$ .	$i_h$ .	$i_h - i_0$ .			
17° 27° 38° 50°	30 60 92 121	69 81 110 130	39 21 18 9			

Since the temperature coefficient of  $i_0$ , is approximately four times as great as the temperature coefficient of diffusion (0·025), it follows that the thickness of the diffusion layer decreases as the temperature is raised. The results in Table VI. show that at the same time the magnitude of the H.F. effect decreases; this is in harmony with the observations made in stirred solutions.

The H.F. Effect and Power Expenditure.—An examination of the results in Tables I., II. and III. indicates that the effect of high frequency

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TABLE VII.—H.F. EFFECT AND POWER IN VARIOUS SOLUTIONS.

Depolariser.	Conen.	Electrolyte.	i <sub>0</sub> .	i <sub>h</sub> .	Р.	k.
Cathodic.						
Pot. Ferricyanide .	0.002 M 0.005 0.01 0.01 0.01 0.01 0.01 0.01	0·1 N-NaOH  ''  0·04 N-NaOH  '', + 0·2 M-Na <sub>2</sub> SO <sub>4</sub> 0·01 M-Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> '', + 0·2 M-Na <sub>2</sub> SO <sub>4</sub> 0·1 N-NaOH	4·1 9 17 16 16 16 14 38	19 36 65 85 54 79 56	0.47 0.46 0.44 0.85 0.30 0.71 0.36	13·5 11·3 11·0 11·9 11·1 12·0 12·7 8·5
Ferric Alum .	0.002 M 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.0	$\begin{array}{c} \text{o:I } N\text{-}\text{H}_2\text{SO}_4 \\ N\text{-}\text{H}_2\text{SO}_4 \\ \text{o:2 } N\text{-}\text{H}_2\text{SO}_4 \\ \text{o:I } N\text{-}\text{H}_2\text{SO}_4 \\ \text{o:I } N\text{-}\text{H}_2\text{SO}_4 \\ \text{o:O4 } N\text{-}\text{H}_2\text{SO}_4 \\ \text{::} + \text{o:O5 } M\text{-}\text{Na}_2\text{SO}_4 \\ \text{::} + \text{o:I } M\text{-}\text{Na}_2\text{SO}_4 \\ \text{::} + \text{o:2 } M\text{-}\text{Na}_2\text{SO}_4 \\ \text{::} + \text{o:5 } M\text{-}\text{Na}_2\text{SO}_4 \\ \text{::} + \text{o:M}_2\text{SO}_4 \\ \text{::} + \text{o:O6 } C_2\text{H}_5\text{OH} \\ \text{o:I } N\text{-}\text{H}_2\text{SO}_4 \\ \end{array}$	3.0 12 12 12 12 12 12 12 12 10 10 12 27	13.5 28 43 54 78 64 55 49 36 80 105 132	0.43 0.070 0.24 0.42 0.93 0.67 0.52 0.36 0.23 1.78 2.03 0.41	13.5 12.9 13.4 13.8 13.9 13.5 12.7 13.0 13.8 13.4 12.8
Pot. Permanganate	0.0004 M 0.0004 M 0.004 0.004 0.01	o·I N-NaOH o·I N-H <sub>2</sub> SO <sub>4</sub> o·I N-NaOH o·I N-H <sub>2</sub> SO <sub>4</sub> o·I N-NaOH	3:5 6:1 36 53	13·5 27 152 217 361	0.44 0.42 0.43 0.42 0.44	11·1 13·6 12·6 12·3 9·1
Quinone	0.001 M 0.005 0.01	o·1 <i>N</i> -H₂SO₄ ,,	4.4 18 36	18·5 89 167	0·43 0·43 0·42	12·3 15·3 14·3
Cadmium Sulphate	0.005 M	Acetate buffer	15 41	4I 132	0.18 0.18	13.4
Copper Sulphate	0.001 M 0.005 0.01	o·ı N-H₂SO₄	3·0 20 39	12·5 66 129	0·43 0·42 0·42	9·1 9·1
Anodic. Pot. Ferrocyanide .	0·002 M 0·01 0·02	o·1 <i>N</i> -NaOH ,,	2·4 17 37	11 59 124	0·47 0·44 0·43	13·3 9·6 9·2
Ferrous Sulphate	0.002 M 0.01 0.02	0·1 N-H <sub>2</sub> SO <sub>4</sub>	2·4 12 26	10 53 121	0.43 0.42 0.41	13·5 15·1
Iodine	0.001 M 0.005 0.01	o·I N-H <sub>2</sub> SO <sub>4</sub>	3·0 23 48	15 80 158	0·43 0·43 0·42	15·5 9·6 9·0
Hydroquinone .	o·oɪ M	o·1 N-H <sub>2</sub> SO <sub>4</sub>	30	150	0.42	15.8
Hydroxylamine	0.01 M	o·I N-H <sub>2</sub> SO <sub>4</sub>	115	417	0.42	10.4

oscillations on the limiting current, for a given depolariser at least, might be represented by an equation of the form

$$\frac{i_h - i_0}{i_0} = khf(R) \qquad . \qquad . \qquad . \qquad (i)$$

where k is a constant, h the high frequency current strength, and f(R) is a function of the resistance of the electrolyte. It appeared possible at first that f(R) might be equal to R, when the high frequency effect, as measured by  $(i_h-i_0)/i_0$ , would be proportional to Rh, that is to the high frequency E.M.F. Experimental studies in solutions of various resistances showed, however, that this supposition was incorrect and it appeared more probable that f(R) was equal to  $\sqrt{R}$ ; the high frequency effect should then be proportional to  $h\sqrt{R}$ , that is to  $\sqrt{Rh^2}$ . Since the product of the resistance and the square of the current is a measure of the power (P) expended in the cell, which is practically non-inductive, it follows that a probable relationship is

$$\frac{i_{h}-i_{0}}{i_{0}}=k\sqrt{P} \qquad . \qquad . \qquad . \qquad (ii)$$

Although this equation was satisfactory when using the same electrode throughout, the value of the constant changed when the electrode was changed, and the equation

$$\frac{i_h - i_0}{i_0} = k\sqrt{P/A}$$
 . . . (iii)

where A is the area of the test electrode, was finally adopted as being in excellent agreement with the observations, as the results in Tables VII. and VIII. show. The high frequency power was determined by measuring the heat evolved during the passage of high frequency current through a given volume of electrolyte; <sup>7</sup> the values of P quoted and  $i_h$  were measured with 125 milliamps. of high frequency current. Table VII. gives the results for various depolarisers, both anodic and cathodic, which react rapidly at the electrode, using a test electrode of 6·5 sq. mm. area; the results in Table VIII. are for a constant depolariser (0·01 M-ferric alum in 0·1 N-sulphuric acid) with electrodes of various areas. The last column of each Table gives the value of k according to equation (iii), P being expressed in watts and A in sq. mm.

Area (sq. mm.).	$i_0$ .	<i>i</i> <sub>h</sub> .	P.	k.
2·7 6·5 8·7 15·7 38·6	6·7 12 18 27 63	48·5 52·5 62·5 69	0·785 0·437 0·327 0·219 0·090	11·5 13·0 12·7 12·9 12·8

TABLE VIII.-H.F. EFFECT AND ELECTRODE AREA.

#### Discussion.

Although there is some variation in the "constant" k, it appears very probable that equation (iii) represents in general the influence of the high frequency oscillations on the limiting current over a wide range of conditions, both at an anode and a cathode, irrespective of the nature of the electrode process. In some cases, e.g., when the depolariser is potassium permanganate or ferricyanide, the value of k appears to decrease with increasing concentration; no doubt the ions present produce secondary effects in these instances, which disappear as the dilution of the solution is increased. Since the H.F. effect does not depend on the material of the electrode, or whether it is an anode or a cathode, it appears that the origin of the effect is not specific to the test electrode; a number of observations made in the course of the present work indicate that the value of k is also independent of the size and position of the high frequency spiral electrode.

The H.F. effect on the limiting current, as measured by the expression  $(i_h - i_0)/i_0$ , apparently depends only on the power expended per unit area of the test electrode, and this fact suggests that the high frequency currents produce their effects, both on the limiting current and on potential (see Part I.), by causing a mechanical disturbance in the vicinity of the electrode; such a disturbance would have the effect of increasing the rate at which material diffuses to the electrode and would account for the observed facts. It was at first thought possible that the origin of the mechanical disturbance lay in the convection currents which would result from local heating at the test electrode brought about by the high frequency oscillations, but this simple view was abandoned as a full consideration of the facts showed there was no reason to believe that the rise of temperature in the vicinity of the electrode would be greater than that in the bulk of the electrolyte. The temperature of the latter never rose more than a degree or two during the course of an experiment, and such a rise is quite incapable of producing the effects observed.

The only factor which is common to all the experiments made in the course of verifying equation (iii) is the water used as solvent, and the origin of the H.F. effect may lie in the disturbance resulting from the oscillation or rotation of the molecular dipoles of water caused by the application of a rapidly alternating field. This might have an influence similar to that of stirring the electrolyte, that is to decrease the effective thickness of the diffusion layer and so to increase the limiting current; the relative increase might reasonably be expected to be directly related, as has been actually found, to the high frequency power expended in the solution per unit area of the electrode. This mechanism would also account for the decrease of the H.F. effect observed in stirred solutions (Table V.) and at elevated temperatures (Table VI.). The theory that the H.F. effect is due to the disturbance resulting from the oscillation of dipole molecules could be tested by experiments with alternations of frequencies of the order of  $10^{10}$  per second; under these conditions the "relaxation time" of the molecules would be greater than the time between two successive pulses of current and the molecules would not rotate in the electrical field.9 Unfortunately the experimental diffi-

<sup>&</sup>lt;sup>8</sup> Ref. (1), see B, Fig. 2.
<sup>9</sup> Debye, "Polar Molecules," 1929, Chap. V.; Smyth, "Dielectric Constant and Molecular Structure," 1931, Chap. II.

culties in the design of an oscillator capable of producing the necessary energy to test this point are so great as to preclude the authors from

continuing the work for the present.

It is interesting to note that Brunner 10 and others have found that when a solution is stirred the limiting current is increased approximately according to the two-thirds exponent of the rate of, and hence the power expended in, rotation. A similar relationship might have been expected between the H.F. effect on the limiting current and the high frequency power expenditure, and the difference between the exponents of twothirds and the one-half, actually observed, may be due to the introduction of subsidiary factors in connection with the H.F. effect.

#### Summary.

(I) A study of the effect of high frequency oscillations on the limiting current for 100 per cent. electrode efficiency shows that the H.F. effect cannot be due to its influence on the chemical reaction at the electrode, but is related to an increase in the rate of diffusion of the depolariser.

(2) The relative H.F. effect on the limiting current is found to be independent of the surface tension of the electrolyte, although it is increased by an increase of viscosity; stirring the solution or raising its temperature

decreases the effect.

- (3) The addition of neutral salts increases the conductance of the electrolyte used and at the same time brings about a marked decrease in the H.F. effect; this observation has been accounted for by showing that under a very wide variety of conditions the relative H.F. effect on the limiting current is proportional to the square root of the power expended in the solution per unit area of electrode surface.
- (4) The H.F. effect is probably brought about by a mechanical disturbance in the electrolyte; this cannot be due to local heating at the electrode, but may be caused by the oscillatory rotation of the molecular dipoles constituting the water used as solvent.

The University, Sheffield.

<sup>10</sup> Brunner, Z. physikal. Chem., 47, 56, 1904.

#### ON THE INSTABILITY OF THICK FILMS OF IN-SOLUBLE OILS ON WATER.

By C. G. P. FEACHEM AND ERIC K. RIDEAL.

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It has long been known that a thick film of an insoluble oil on a water surface is unstable and breaks up into a number of lenses or drops floating on the surface. The phenomenon has been described by Rayleigh,1 Hardy,2 and in detail by Taylor.3 McTaggart 4 directed a microscope on to a Langmuir trough and observed the formation of small drops of

<sup>1</sup> Lord Rayleigh, Collected Works, 3, 424.

W. B. Hardy, Proc. Roy. Soc., 86A, 612, 1912.
 W. Taylor, A New View of Surface Forces, Toronto Press, 1925.
 H. A. McTaggart, Trans. Roy. Soc. Canada, (3) 23 (3), 153, 1929.

oleic acid when a film of this substance was compressed to its maximum value; on further compression more oil is squeezed into the drops.

From the contours of small lenses investigated by Lyons, we may assume that they may be regarded as spheres; denoting the surface tensions of the oil-air, water-air, and oil-water interfaces by  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_{12}$ , the radius of any drop by r, and the thickness of the original film of oil by D, the observations of Cary and Rideal  $^6$  indicate that the final equilibrium state of the thick film will be a drop or number of drops in equilibrium with a monolayer of oil of thickness  $\delta$  and uniform spreading pressure F.

We can now investigate the conditions under which a thick film will break up into a number of drops of equal size in equilibrium with a monolayer so that the change in free energy is a minimum, i.e., zero, thus giving a minimum or limiting size of drop.

By Antonow's rule we obtain

and the free surface energy of a thick film will be

$$\Delta A_1 = \sigma_2 \quad . \qquad . \qquad . \qquad . \qquad (2)$$

If the thick film now breaks up into n equal drops per unit area separated from one another by a monolayer, we obtain

$$D = n \cdot \frac{4}{3}\pi r^3 + \delta(1 - n\pi r^2), \qquad . \tag{3}$$

whence

$$n = \frac{D - \delta}{\frac{4}{3}\pi r^3 - \pi r^2 \delta}. \qquad (4)$$

The surface energy of this new film will be

$$\Delta A_2 = n \cdot 2\pi r^2 (\sigma_{12} + \sigma_1) + (1 - n \cdot \pi r^2) (\sigma_2 - F)$$
  
=  $n \cdot 2\pi r^2 \sigma_2 + (1 - n\pi r^2) (\sigma_2 - F)$  . . . (5)

whence the decrease in free surface energy will be

$$\begin{split} \Delta A_1 - \Delta A_2 &= (\mathbf{I} - n \cdot 2\pi r^2)\sigma_2 - (\mathbf{I} - n \cdot \pi r^2) \left(\sigma_2 - F\right) \\ &= F - n \cdot \pi r^2 (\sigma_2 + F) \quad . \quad . \quad . \quad (6) \end{split}$$

Now from (4) 
$$n \cdot \pi r^2 = \frac{D - \delta}{\frac{1}{2}r - \delta} \qquad . \qquad . \qquad . \qquad (7)$$

which decreases as r increases. Consequently in (6) the second term, which is negative, increases; thus, at some value of r,

$$\Delta A_1 - \Delta A_2 = 0.$$

This condition is fulfilled when

$$n \cdot \pi r^2 = \frac{F}{\sigma_2 + F} \qquad . \qquad . \qquad . \qquad . \tag{8}$$

Substituting in (4) and neglecting  $\delta$  in comparison with D we obtain

$$r = \frac{3}{4}D\frac{\sigma_2 + F}{F}. \qquad . \qquad . \qquad (9)$$

C. G. Lyons, J. Chem. Soc., (i), 623, 1930.
 Cary and Rideal, Proc. Roy. Soc., 109A, 318, 1928.

This equation (9) gives us the smallest value of the radius r of the drops into which a film can break without an increase in free energy of the

system.

Inserting for oleic acid on water the values  $\delta = 18.5$  Å. F = 30 dynes/cm. and  $\sigma_2 = 70$  dynes/cm. we obtain the following values of n and r for various thicknesses of oil.

TA	BL	Æ	Ι.

D No. of Molecular Layers.	Thickness in Microns.	r in Microns.	No. of Drops per μ <sup>2</sup> .
20 50 90 150 300 500	0.037 0.094 0.167 0.278 0.56 0.93 1.85	0°09 0°14 0°42 0°72 1°40 2°32 4'63	10·9 1·75 0·56 0·198 0·049 0·018

The film may, of course, break up into drops larger than indicated by the above table of minima, and coalescence of the drops may occur. It is, therefore, necessary to consider the relative lives of drops of various sizes. Preliminary investigation revealed the fact that when a film contains both small and large drops embedded in the monolayer, the small drops get smaller whilst patches of open film appear round the large ones; suggesting, like in the analogous case of three dimensions, that the spreading pressure of small drops is greater than that of a large one.

If we consider unit area of film containing n small drops each of radius r and one larger drop which can absorb oil without appreciably altering its surface, the respective spreading pressures of the large and small drops being F and  $F + \Delta F$ , then if the small drops each of radius r decrease in radius by  $\Delta r$  the change in surface energy is given by:

$$\Delta A = n \cdot 2\pi r (\sigma_2 - F) \Delta r - n \cdot 4\pi r \sigma_2 \cdot \Delta r$$

$$= -n \cdot 2\pi r (\sigma_2 + F) \Delta r \qquad . \qquad . \qquad (10)$$

The excess spreading pressure F of each drop acting across a circumference of length  $2\pi r$  has pushed the film away a distance  $\Delta R$ , so that the volume of oil extruded from each drop has formed a ring of film round it of width  $\Delta R$  and thickness  $\delta$ .

$$2\pi r \cdot \delta \Delta R = 4\pi r^2 \Delta r$$
 . . (11)

Now the work expended in spreading due to  $\Delta F$  must be equal to the loss of energy of the drop. Hence from (10) and (11)

$$n \cdot 4\pi r^2 \Delta r \Delta F = n \cdot 2\pi r (\sigma_2 + F) \delta \Delta r$$

whence

$$\Delta F = \frac{\sigma_2 + F}{2} \frac{\delta}{r} \quad . \quad . \quad . \quad (12)$$

which gives us an expression for the additional spreading pressure possessed by a small drop and is, as we note, proportional to the curvature at the edge of the drop. We may thus regard the circular line at the intersection of the three phases as in tension with a tension of k dynes,

where

$$k = \frac{\delta}{2}(\sigma_2 + F) \quad . \qquad . \qquad . \tag{13}$$

For oleic acid on water with  $\delta=18.5$  Å. F=30 dynes/cm. and  $\sigma_2=70$  dynes per cm.,  $k=9\times 10^{-6}$  dynes.

A strip of water of four molecules or 13 Å, wide would possess a surface energy of  $9 \times 10^{-6}$  ergs. per cm.<sup>2</sup>, thus the tension  $k = 9 \times 10^{-6}$  dynes is of the order that the molecular forces concerned might be expected to produce.

The above considerations indicate that small drops should decrease in volume at the expense of large ones, and we must now enquire into the rate of conversion.

If a unifilm of oil of radius R spreads on the surface of water, Land and Volmer 7 showed that its rate of spreading is given by:

$$\dot{R} = \sqrt[3]{\frac{4F^2}{(1\cdot327)^2l\eta\rho}} = \frac{4\cdot28}{\sqrt[3]{R}} \text{ cms./sec.}$$
 (14)

and found experimentally that  $\dot{R}R^3$  was in fact constant.

The small drop of oil in the film is spreading by virtue of its excess spreading pressure  $\Delta F$  hence (14) becomes

$$\dot{R} = \frac{4 \cdot 28}{\sqrt[3]{R}} \left(\frac{\Delta F}{F}\right)^{\frac{2}{3}} \quad . \tag{15}$$

If the disc of radius R is  $\delta$  cm. in thickness the rate of spread of material is given by

$$\dot{\omega} = 2\pi \delta R \dot{R} \text{ cc./sec.} \quad . \qquad . \qquad . \qquad . \tag{16}$$

so that the drop decreases in radius at a rate  $\dot{r}$  given by

$$-4\pi r^2 \dot{r} = \dot{\omega} = 2\pi R \delta \dot{R} \quad . \qquad . \qquad . \qquad . \tag{17}$$

On substituting for  $\mathring{R}$  and for  $\Delta F$  we obtain

$$\dot{r} = -\frac{42.8R\delta}{2\sqrt[3]{R}} \left(\frac{\delta}{2} \cdot \frac{F + \sigma_2}{-F}\right)^{2/3} r^{-8/3} \qquad . \tag{18}$$

$$= -C^{-1} \cdot R^{+2/3} r^{-8/3}$$

or  $dt = -CR^{-2/3}r^8$ 

$$dt = -CR^{-2/3}r^{8/3}dr$$
 . . . (19)

so that the time taken for a drop to disappear is given by

$$t = -CR^{-2/3} \int_{r}^{0} r^{8/3} dr = c'R^{-2/3} r^{10/3} \qquad . \tag{20}$$

Consider two drops of radii  $r_1=10^{-5}$  cm.  $r_2=10^{-4}$  cm. Each may be considered as occupying a circular area of unifilm, of radius R. This radius can be found from column 4 of Table I., for  $4\pi R^2$  is the recip-

rocal of the number of drops per unit area. Hence  $R_1=1.8$  10  $^{-5}$  cm. and  $R_2=1.8$  10  $^{-4}$  cm., hence

$$\frac{t_2}{t_1} = \frac{R_2^{-2/3} r_2^{10/3}}{R_1^{-2/3} r_1^{10/3}} = 10^4 \qquad . \qquad . \qquad . \qquad (21)$$

Consequently, a drop of one micron radius will last ten thousand times longer than a drop with radius o-1 micron.

# Experimental.

Drops formed by films of oleic acid at room temperature were observed with a microscope and a Zeiss-Siedentopf cardioid dark-field condenser, in the manner suggested by Zocher and Stiebel.<sup>8</sup> The films were spread from petrol-ether solution with an Agla micrometer-syringe, on to water in a large, shallow brass trough, standing in a box to avoid draughts.

The surface could not be observed until after the film had been applied for a few seconds; it then appeared fairly evenly covered with drops of radii about one micron, showing small Brownian movement, and drifting at about 0.01 cm. per sec. across the field of view. Interspersed among the drops were more or less circular patches with no small drops. These had a radius of from a half to one millimetre and in the centre of each patch was a large drop, with a radius of 20 to 30 microns.

The rate of drift of the film was such that several such large drops passed across the field of view each minute, and though they varied in size, their general appearance was the same. As the system was observed, its appearance slowly changed. After about an hour, the large drops had grown larger, and each was surrounded by an area of open water, which had also grown larger, its radius being about one millimetre. These areas occupied most of the surface, and were separated by a network of film containing small drops. The strips of this network were about half a millimetre wide, immediately between two open areas. Along the centres of these strips, the small drops kept their original sizes (radii about I micron), but the radii decreased towards the edges of the strip, so that each large area of open water was surrounded by a ring of very small drops, with more drops increasing in size, at greater distances from the open area. It seems clear that this is due to the small drops spreading into the film, and their material passing into the large drops.

When the original film was about 500 layers thick, most of the oil applied was observed to collect into a few very large drops, several millimetres in diameter, and the general appearance of the rest of the film was the same as for thinner films. With a view to investigating the drift of the surface referred to above, a small box with a glass cover, about 10 cm. square, was made to fit tightly round the stage of the microscope, gripping it with flanges covered with velvet. The smallest available Petri-dish was used as a trough, and the objective of the microscope projected through a small hole in the glass cover, and after adjustment it was sealed in by means of a strip of cellophane. This was quite free from draughts, and dust-particles on the surface of the water kept quite still for several minutes, yet, as soon as a film was applied, it broke up into drops, which started drifting as before. This suggests that various very big drops are absorbing oil and the film is being pushed towards them, by the greater spreading-pressure of the smaller drops.

<sup>8</sup> H. Zocher and F. Stiebel, Z. physik. Chem., 147A, 401, 1930.

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The eye-piece of the microscope had a grid of 400 squares in it, with which the sizes of drops could be measured and their number counted. The results are set out in Table II. The fourth column gives the diameters of the drops, evaluated roughly with reference to the squares of the grid. This can only be approximate, as a drop of radius two microns is almost too small for a microscope to give a good image, as opposed to a diffraction pattern. The fifth column gives the diameters of the drops, calculated on the assumption that each is a sphere, and contains all the oil which was originally in the area of film now occupied by the drop: (that is to say, the area given by dividing any area by the number of drops in it). The sixth column gives the diameter calculated from the equations leading to Table I., the minimum diameter to be expected.

TABLE II.

Thickness of	Number of	Number of	Observed	Calculated	Calculated
Film Applied.	Molecular	Drops	Diameter	Diameter	Diameter
Microns.	Layers.	Counted.	Microns.	A.	B.
0.018	10	83	$   \begin{array}{c}     1-2 \\     \frac{1}{2}-2\frac{1}{2} \\     2-5   \end{array} $	1.58	0°045
0.034	19	43		2.46	0°085
0.041	39½	<i>ca.</i> 120		5½	0°19

It will be noted that the smallest drops observed are about ten times as large as the smallest permitted by the potential-energy theory above, and these were disappearing at such a rate that those nearest the big drops probably had a life of about an hour. Consequently, from equation (21) above, the small ones, if they were ever formed would only last about  $\frac{1}{3}$  second, and so never be seen.

The volume of the drops observed was assumed to be equal to the volume of oil originally in that area of the thick layer occupied by each drop. This is approximately justified by some observations made on the large drops, which are set out in Table III.

TABLE III.

Observation Number.	Thickness of Film Microns.	Area of Empty Surface Containing One Large Drop.	Observed Diameter, Microns,	Calculated Diameter. Microns.
1 2 3 4 5	0.034 ,, 0.024 0.021	20 squares 28 ,, 8 ,, 250 ,, circle radius 8 sq. circle radius 3½ sq.	12 20 8 60 35½ 26½	12.4 15.6 10.3 37.0 38.0

The agreement between columns 4 and 5 of Table III., excepting observation 4, justified this assumption, likewise the values in column 5 of Table II., to about 10 per cent.

It was, of course, desired to continue observations of films for periods of several hours, but this could not be done, owing to a change occurring in the film, which appeared to solidify. The drops lost their Brownian

movement, and the film ceased to drift, and began to show a faint, crystalline appearance; when displaced a little, it returned to its original position, and crystals began to grow inside the larger drops. The authors have not found the cause of this; it may be due to a change occurring, such as oxidation of the oleic acid, or to solution of the wax from the edges of the trough into the film, but it prevents long observations on one film.

In conclusion, though it has been shown not to be surprising that the smallest possible drops are not observed, there remains the fact that, at first, all the drops of about one micron radius were very uniform in size. If the 0·1  $\mu$  drops ever formed, they would have disappeared before observation began, but it may be that drops form on nuclei, such as dust or ions in the air which strike the surface, and that the number of these nuclei determines the number, and so the radius, of the small drops first formed.

#### Summary.

Potential-energy considerations are applied to determine the size of the smallest drops into which a thick film of oleic acid on water will break, the excess of the spreading-pressure of small drops over that of big ones, and the relative lives of small drops of different sizes in the presence of big drops.

The appearance and behaviour of a broken-up film are described.

Counting and measurement show:

(r) That each drop contains the excess oil in that area of film which it may be said to occupy.

(2) That small drops decrease in size, and pass the oil in them into

big drops.

(3) That the smallest drops observed are some ten times larger than the smallest permitted, but that the latter, if ever formed, would only have a life of about one-third of a second.

The authors wish to express their gratitude to the Department of Scientific and Industrial Research and to the Master and Fellows of Clare College for giving a maintenance grant and a Research Studentship respectively to one of them (C. G. P. F.) which made this work possible.

# THE DISSOLUTION OF MAGNESIUM IN AQUEOUS SALT SOLUTIONS. PART I. EFFECT OF IMPURITIES.

By L. WHITBY.

Received 17th November, 1932.

Considerable work has been done in measuring the rate of dissolution of magnesium in salt solutions; 1 no attention has been given, however,

<sup>1</sup> Lemoine, Compt. rend., 129, 291, 1899; Tommasi, Bull. Soc. chim. (3), 21, 885, 1899; Kahlenberg, J.A.C.S., 25, 380, 1903; Roberts and Brown, ibid., 25, 801, 1903; Getman, ibid., 38, 2594, 1916; 39, 596, 1917; Hughes, J.C.S., 115, 272, 1919; Portevin and Pretet, Rev. Met., 26, 259, 1929; Bekier and Zablocki, Rocz. Chem., 10, 314, 1930; Endo and Miyazaki, J. Study Met., 7, 283, 1930; Iitaka, Proc., Imp. Acad. Tokyo, 6, 363, 1930; Schilov and Schatunovskaja, J. Russ. Phys. Chem. Soc., 62, 373, 1930.

to the effect of the varying traces of impurities usually present in commercial (99.90 per cent.) magnesium.

The results recorded in the present communication show that if reproducibility is desired such impurities cannot be neglected, and suggest that the results of previous workers possess little value owing to failure to investigate this question adequately.

#### Experimental.

Magnesium sheet of about 99.90 per cent. purity was obtained from the American Magnesium Corporation. Four distinct batches of metal were separated by means of their different thicknesses (0.20, 0.19, 0.18 and 0.16 mm.). A small quantity of redistilled metal, received through the courtesy of Mr. W. R. D. Jones of University College, Cardiff, was rolled down at 100° C., to approximately 0.4 mm. thickness, beyond which it was not found practicable to roll.

Samples of each material, after washing in acetone redistilled from anhydrous sodium sulphate, were cleaned by a steel scratch brush; loosely adherent metal was removed by cotton wool dried at 100° C. Spectrograms of the material so prepared were obtained by permission of the Superintendent of the Metallurgical Department (N.P.L.). Spark spectra taken on a Type E1 Hilger quartz spectrograph enabled an approximate estimate of the amount of each impurity to be made from the number of lines visible. Results are recorded in Table I. A few pieces of metal that were hand polished, finished with an alkaline suspension of alumina and etched with aqueous dilute nitric acid failed under the microscope to show any inclusions.

1000		Mg(R).	Mg(C),	Mg(C1).	Mg(C2).	Mg(C <sub>3</sub> ).
Ca Al		<pre>&lt; 0.003 &lt; 0.003</pre>	0.003-0.01 < 0.003 0.003-0.01 0.01-0.03 0.003-0.01 nil < 0.003 < 0.003 < 0.003 < 0.003 < 0.003 = 0.003 = 0.003 = 0.003	0.003-0.01 <0.003 <0.003 <0.003 <0.003 <0.003 iil nil nil nil <0.003 <0.003 <0.003	0.01-0.03 0.01-0.03 0.01-0.03 0.01-0.03 0.01-0.03 0.003-0.01 0.003-0.01 0.003 0.003 0.003 0.003	0.003-0.01 0.003-0.01 0.01-0.03 0.003-0.01 0.003-0.01 0.003 0.003 0.003 0.003 0.003 0.003 0.003
Thickness m	m.	0•40	0.10	0.30	0.18	0.18

TABLE I.—Spectroscopic Analysis of Metal used.

Specimens were prepared (as described above) for dissolution experiments and were cut to a uniform size of  $1.5 \times 4$  cms. and suspended vertically in a corrosion vessel by a thin glass hook through a punched hole  $\frac{1}{4}$  inch diameter. The corrosion vessel used has been previously described.<sup>2</sup>

Sodium chloride solutions were made from laboratory distilled water, redistilled from alkaline permanganate; Kahlbaum's purest sodium

<sup>&</sup>lt;sup>2</sup> Trans. Faraday Soc., 28, 474, 1932.

chloride was used. Experiments were conducted at 25° C., in an electrically controlled thermostat; 50 c.cs. of solution were always used and were introduced by the method described previously <sup>2</sup> after complete thermal equilibrium had been reached.

Annealing of specimens was carried out after first cleaning, cutting, punching and packing in several layers of clean magnesium foil and then placing in a pyrex tube fitted with ground stopper and tap. The tube was evacuated by a two stage Hyvac pump and placed for about 3 hours in an electric tube furnace heated to 350° C., after which current was switched off and the tube allowed to cool in the furnace; the pump was kept working continuously. Specimens annealed in this way appeared quite bright on removal.

Measurement of Dissolution.—Work by other investigators, together with analytical experiments conducted by the writer over long time intervals 2 have shown that the attack of magnesium by both concentrated and dilute sodium chloride solutions is represented entirely by hydrogen evolution. Hydrogen was accordingly measured by open-end capillary manometers, both a water-filled and a mercury-filled manometer being connected to each corrosion vessel via a two-way capillary tap. The initial stages of the reaction could be followed by reading the water manometer, the mercury manometer being used only in case of rapid hydrogen evolution or of long periods between readings. Periodically the key of the connecting tap was removed and replaced, thus equalising the pressure with that of the atmosphere.

The average internal volume of the capillaries was measured by water weight and a volume correction introduced for each reading; effect of pressure on the manometer volume was neglected. Atmospheric pressure was corrected for, the barometer being read with each manometer reading.

The bore of the capillary was about 1.5 mm. and surface tension differences were at first feared; Table II., however, shows the results of

	No. of Manometer Readings.		c.cs. H <sub>2</sub> (N.T.P.)		
Weight of Mg g.	H <sub>2</sub> O.	Hg.	Theoretical.	Calc. by Manometer.	
0°1754 0°1800 0°1728 0°1788	2 1 1	5 12 11 10	161*5 165*7 159*1 164*6	162*4 166*0 158*3 164*1	

TABLE II.

some experiments that were taken to completion and indicates the accuracy of the method. The number of manometer readings is that number between each of which the pressure was released.

Reproducibility of Results.—For clarity all results are plotted as the mean of the number of experiments performed. Usually experiments were duplicated but sometimes four or six experiments were made over the initial stages of the attack. Table III. shows percentage variations of sets of duplicates from the mean at increasing times from commencement of the reaction. These figures are taken first from three cases where reproducibility, at first bad, has afterwards improved and

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then from two typical cases; an interpretation of these results is given later. After the first few hours duplicates usually showed agreement to within  $\pm$  2 per cent. from the mean.

IADLE III.	EFFECT OF TIME	ON REPRODUCIBILITY OF	MESULIS.
Strength of Sodium Chloride Solution.	Magnesium.	Time.	Per Cent. A.
N/10	Mg (C2)	ro mins. r hr. 6 hrs.	11°1 7°9 3°3
N/10	Mg (C1)	10 mins. 1 hr. 6 hrs.	25°5 19°1 4°1
N/10	Mg (R)	10 mins. 1 hr. 6 hrs. 24 "	47°2 25°7 9°4 5°5
N/I	Mg (C)	Io mins. I hr. 6 hrs. I2 " 24 " 48 ",	6·1 9·0 3·9 1·7 1·2 1·3
3N	Mg (C1)	10 mins. 1 hr. 6 hrs. 12 ,,	0°0 4°8 4°7 2°1

TABLE III .- EFFECT OF TIME ON REPRODUCIBILITY OF RESULTS.

Distribution of Corrosion.—A freshly cleaned specimen after immersion in sodium chloride solution rapidly evolves hydrogen from innumerable points sporadically distributed over the surface. After a few minutes the number of points materially diminishes and the interstices exhibit a yellowish brown interference colour. After about one hour hydrogen comes from a few points only which appear as bunches of thin black lines, the interstices between these bunches in the meantime, become covered with a thicker brownish-yellow film showing a thin loose layer of magnesium hydroxide. It is noteworthy that a similar film may be produced on magnesium by immersion in a warm saturated solution of magnesium hydroxide; if the magnesium is made cathodic to the solution the film forms with greater ease. Sodium hydroxide solution gives no visible film. Electrophoretic deposition of magnesium hydroxide sol probably plays a part in the mechanism of this film formation.

The distribution of corrosion after a few hours (by which time the bunches of black lines change to black patches) remains without material alteration, dissolution continuing at the black patches until the metal is penetrated, after which attack continues by undercutting the film covered areas. The attacked areas were always small compared with the unattacked, film covered, areas (about 30 per cent.); variations in the number and size of the black dissolving areas determine the large variations in rate of attack exhibited by the different samples.

It was noticed that hydrogen appeared to come from the dissolving parts of the metal, a fact already noticed to occur with zinc by Bengough

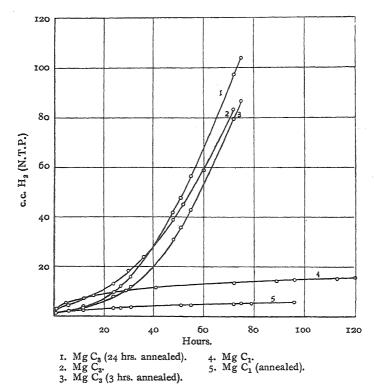


Fig. 1.—Effect of annealing on rate of solution in N/50 sodium chloride solution.

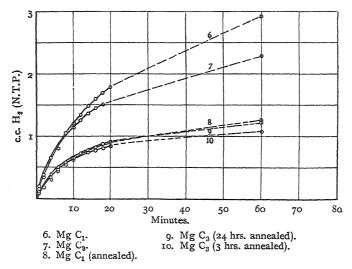


Fig. 1A.—Effect of annealing on initial rate of dissolution in N/50 sodium chloride solution.

and colleagues.3 Hydrogen formation at the dissolving parts of the

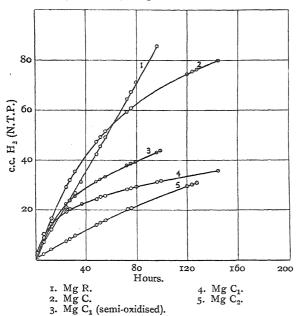


Fig. 2.—Dissolution/time curves in N/10 sodium chloride solution.

surface is not compatible however with the electrochemical theory of corrosion (separate anodes and cathodes), and it is suggested, therefore, that hydrogen actually discharged as near the boundary between cathodic and anodic parts of the surface as possible. since at these parts the lines of force densest; will be bubble formation will then occur at the most suitable, i.e., the roughest, parts of the adjacent surface, which will be the anodes.

### Influence of

**Strain.**—The effect of annealing was tried on samples of Mg (C<sub>3</sub>) and Mg (C<sub>1</sub>); results of dissolution in N/50 sodium chloride solution of

annealed and of " as received " samples of both materials shown in Figs. 1 and Ia. Reduced action occurs after annealing, being more during marked the initial stages of the reaction; such reduction persists, however, with Mg (CI).The results show that the large variations in the of rate attack are not due to differences in the degree of working,

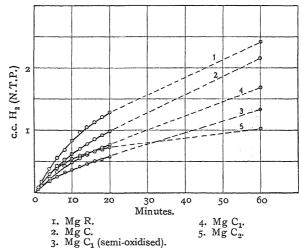


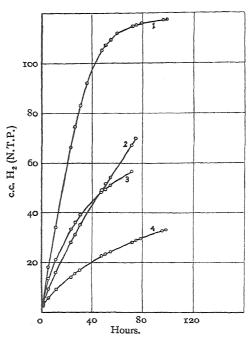
Fig. 2A.—Dissolution/time curves in  $N/\rm ro$  sodium chloride solution. Initial action.

although a slight increase in the rate may be caused by the presence of strain.

acceleration The attack with time exhibited by Mg C3 indicates a progressive deposition of a noble impurity; after 70 hours Mg C3 had dissolved six times as much Mg (CI). The only impurity present to an appreciably greater extent in Mg (C<sub>3</sub>) is manganese, which must, therefore, be deposited as oxide, hydroxide or basic salt; acceleration of attack may then take place by progressive formation of local between couples magnesium and magnesium ennobled by deposition of a manganese compound. action of small quantities of manganese is curious since quantities up to 2 per cent. are normally added to magnesium to reduce corrosion. Amounts so large, however, may be

capable of forming a complete protective of an insoluble manganese compound over the surface; immersion of a 2 per cent. manganesemagnesium alloy in sodium chloride solution was found to produce a general darkening of the surface, which confirms this view.

The fact that annealing for twenty-four hours causes an increased attack may be explained by assuming that small quantities of a high manganese



Mg C.
 Mg R.
 Mg C<sub>1</sub>.
 Mg C<sub>2</sub>.
 Fig. 3.—Dissolution/time curves in N/I sodium chloride solution.

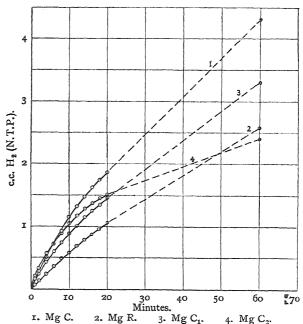


Fig. 3A.—Dissolution/time curves in N/x sodium chloride solution. Initial action.

phase are caused to pass into solid solution by prolonged heat treatment, manganese will then be dissolved by aqueous solutions more readily than when present as minute inclusions of a manganese rich constituent.

Curves showing connection between hydrogen evolution and time during both later and initial stages of the attack for specimens of Mg (R), Mg (C), Mg (C1), and Mg (C2) in N/10, N/1 and 3N sodium chloride solutions are shown in Figs. 2 and 2a, 3 and 3a, and 4 and 4a respectively.

Effect of Impurities.—Although traces of impurities have never before been considered to affect reproducibility of dissolution experiments with magnesium, the extreme difficulty of obtaining a reproducible magnesium electrode has often been noticed 4 and is generally accounted

for by the presence of traces of impurities.

The difficulty of ascertaining the exact function of the impurities in causing such large variations in the attack becomes apparent after a careful study of Table I. and the curves.

The initial action curves show that the differences become apparent The purest metal, rapidly. Mg (R), is not the least attacked but exhibits one peculiar feature—a slight retardation only of the action with time.

In the absence of local impurities the initial p.d. between the dissolving and inert parts of the metal should be small. The secondary p.d. is due probably to ennoblement of the inert parts by a film, which may be deposited electrophoretically as already suggested. The properties

2. Mg R. I. Mg C. 3. Mg C<sub>1</sub>. 4. Mg C2. Fig. 4.—Dissolution/time curves in 3N sodium chloride solution.

of the film will be determined to some extent, therefore, by the cathode potential.

If differences in the rate of attack are determined largely by the properties of the cathode film, dissolution of the metal in a liquid capable of preventing film formation should result in the attack being equalised for all the samples. Fig. 5 records the result of dissolution in N/20hydrochloric acid and amply confirms this view. Differences in the final amount of hydrogen evolution are due to variations in the thickness of the metal.

The diminishing rate during the final parts of the curves in Figs. 2,

<sup>&</sup>lt;sup>4</sup> Neumann, Z. physikal. Chem., 14, 215, 1894; Beck, Rec. trav. chim., 41, 353, 1922; Bodforss, Z. physikal. Chem., 153A, 83, 1931.

3 and 4 is due to penetration of the metal; persistence of the straight line with Mg (R) is due to its greater thickness.

#### Mechanism of the Attack.

The primary sporadic distribution of corrosion which diminishes to attack at few points only is not confined to magnesium but has been noticed by Bengough and co-workers 5 to occur with zinc after immersion in neutral salt solutions. A satisfactory explanation of the disappearance of the primary distribution of the attack has never been given; moreover, the cause of the initial local distribution of corrosion is still

open to speculation. Evans 6 suggests that it is due to weak points in the airformed oxide film. cannot be denied that such a film exists, although under some conditions it is impossible to distinguish between a film of oxide and a layer of gas held to the surface by mirror image forces.

The possibility also exists that initial action occurs by selective ion adsorption at lines of increased adsorption density on the otherwise homogeneous metallic surface. These lines may be caused by crystal surfaces of different crys-

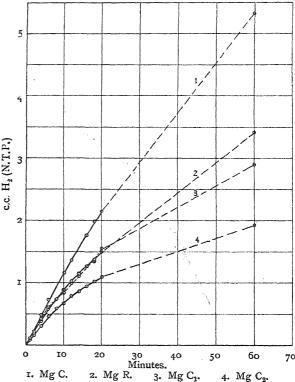


Fig. 4A.—Dissolution/time curves in 3N sodium chloride solution. Initial action.

tallographic orientation or by irregularities produced either mechanically or by disturbances during crystal growth. Pietsch and co-workers? formulated a topochemical theory of corrosion assuming preferential ion adsorption, and Walpert 8 has suggested that the primary act of corrosion consists of ion adsorption.

The explanation of the rapid diminishment of the initial number of points of attack on the corroding metal surface may thus be connected with removal through solution of many of the points conducive to anion

<sup>&</sup>lt;sup>5</sup> Proc. Roy. Soc., 131A, 508, 1931. <sup>6</sup> J.C.S., 92, 111, 1929; Trans. Amer. Electrochem. Soc., 57, 407, 1930. <sup>7</sup> Z. Electrochem. (ii), 37, 823, 1931; Z. physikal. Chem., 157, 363, 1931. 8 Z. physikal. Chem., 151A, 219, 1930.

discharge. Heat treatment in vacuo of a metal of high vapour pressure, such as magnesium, will cause many of the geometric irregularities of the surface to be smoothed off, thus lowering the initial rate of dissolution. Most of the results shown in Figs. I and Ia may be explained on this assumption.

The result of decreasing the number of anodes will be to increase the c.d. at those remaining to such an extent that increased anion drift to these parts occurs which in turn increases the cathode potential and, therefore, the total p.d. built up will be high enough to ensure continuous attack. Another explanation which cannot be ignored is due to the fact that as hydrogen ion discharge occurs the resulting excess of hydroxyl

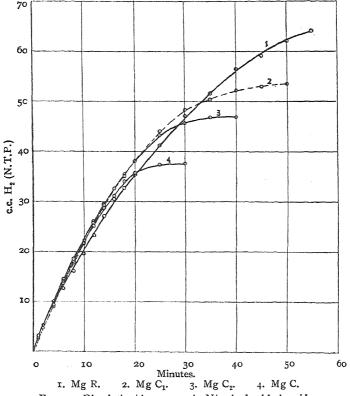


Fig. 5.—Dissolution/time curves in N/20 hydrochloric acid.

ions will drift to the anodes and after reaching a certain critical concentration will be discharged, together with the other anion, resulting in formation of a basic salt, or of an hydroxide, over many of the anodes. Discharge of hydroxide ions in this way results in a surface compound, the solubility relations of which do not conform with those of the same compound in bulk. This fact explains why an insoluble surface compound can form, although the surrounding liquid is unsaturated with regard to that compound in bulk. The effect of this layer will be to shift the interfacial potential in such a direction that these areas become cathodic to the parts still inducing preferential anion discharge, thus raising the c.d. at the latter areas. Meanwhile, the metal ion concentra-

tion in the solution will grow until the solubility product of the metallic hydroxide is reached, when further excess of hydroxyl ions will be

removed by formation of metallic hydroxide.

The potential of the cathode may be considered in the case of magnesium as that due to an oxide electrode with the gas at a pressure equal to the dissociation pressure of the oxide; the final potential difference will hence depend on the formation of a film at the cathodes.

The initial distribution of attack over a chemically homogeneous metal surface may sometimes be due, therefore, to the building up of a p.d. due to properties of the metal which may be entirely removed from

chemical impurities or locally weakened surface films.

Considerable variation would be expected in the number of points initially capable of facilitating anion or cation discharge. On the other hand the average c.d. distribution which ensures the "secondary" distribution of attack on the metal surface will probably be the same for each set of duplicates and will thus ensure better agreement after some hours than during the early stages of the attack—this is the suggested interpretation of the results recorded in Table III.

In Figs. 2 and 2a are shown curves for Mg (CI) which was oxidised by heating to 400° C., for 3 hours and then to 500° C., for 30 minutes. The resulting oxide film was then semi-removed by a few light strokes

with a scratch brush.

The lower rate during the initial stages of the reaction for the semi-cleaned, compared with the fully cleaned, surface, receives the obvious explanation that about half the surface of the former was not functioning normally at this stage, due to the protective film. The increased attack shown by the semi-cleaned specimen during later stages provides confirmation of the view already advanced that the final p.d. is that due to the clean metal and the film covered areas.

#### Summary.

The dissolution of four grades of magnesium, none less than 99.90 per cent. magnesium has been measured in N/10, N and 3N sodium chloride and N/20 hydrochloric acid solutions.

Large variations in rate of dissolution were encountered in sodium chloride solution, and it is considered that duplication of results is impossible

with magnesium unless extremely pure metal is used.

Variations in the rate of dissolution are caused by changes in the type of film formed at the cathodic parts of the surface; dissolution in dilute hydrochloric acid results always in the same rate.

Little difference is shown by hard-worked and fully annealed metal. The presence of about 0 02 per cent. of manganese causes an acceleration of attack with time; in general, the action slows off with time.

A preliminary discussion of the mechanism of the attack is given.

The work has been carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, under the supervision of Dr. G. D. Bengough, to whom the author is indebted for advice and interest; thanks are due to the Chairman, Professor Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, F.R.S., Director of Chemical Research, for permission to publish.

F.R.S., Director of Chemical Research, for permission to publish.

Acknowledgment is also due to Mr. H. R. Sullivan who performed

the spectroscopic analyses.

Chemical Research Laboratory, Teddington, Middlesex.

# THE ELECTRO-DEPOSITION OF IRON-COBALT ALLOYS. PART II.

By S. Glasstone and J. C. Speakman.

Received 23rd November, 1932.

In continuation of the work already reported on the deposition of iron-cobalt alloys from buffered solutions of mixed sulphates of these metals at 16°, experiments have now been made at 50° and 90°. No previous study of the deposition under these conditions appears to have been described.

### Experimental.

The general experimental arrangement was the same as had been used in previous work on the deposition of alloys of the iron-group metals,  $^{1}$ ,  $^{2}$ ,  $^{3}$ ,  $^{4}$ ,  $^{5}$  and the method of analysing the deposits for iron and cobalt was that described in Part I.). As in previous work at elevated temperatures the  $p_{\rm H}$  values of the solutions used were determined at room temperature and a relatively smaller number of deposits than usual was made.

#### Results.

The solutions used in the present work were II, IV, V, VI, VII and VIII of Part I.¹ The compositions of the alloys obtained from each solution at a series of current densities were plotted on a graph and a smooth curve drawn through the points so obtained; the resulting curves are shown in Fig. 1 (50°) and Fig. 2 (90°), and should be compared with those bearing the same Roman numerals in Part I.

#### Discussion.

It will be seen from curves II, VI and VIII in Fig. 1, which represent the compositions of the alloys deposited from solutions containing 50 per cent. of the total metal as iron at  $p_H$ 's of 3·2, 4·0 and 5·2, respectively, at 50°, that the maximum proportion of iron in the deposits obtained at high current densities is independent of the hydrogen ion concentration of the electrolyte. This conclusion is in agreement with that reached from the work on the deposition of iron-cobalt alloys at ordinary temperatures, and of the other alloys of the series at all temperatures. The tendency, observed in previous work, for the deposits to attain a constant composition as the C.D. is increased is clearly seen in Fig. 1; the origin of this effect has already been discussed, and it has been attributed to the compensation of three factors, viz., (a) retarding effect of iron on the deposition of cobalt, (b) local depletion of ferrous ions in the electrolyte, and (c) depolarisation of cobalt deposition by

<sup>&</sup>lt;sup>1</sup> Trans. Faraday Soc., 28, 733, 1932.

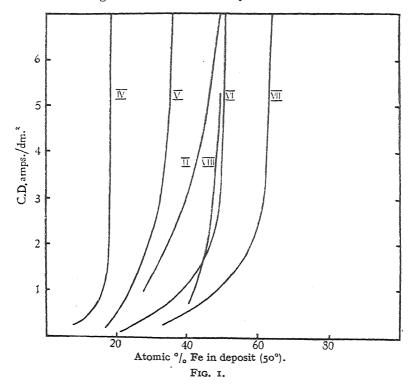
<sup>&</sup>lt;sup>3</sup> *Ibid.*, **24**, 370, 1928. <sup>5</sup> *Ibid.*, **27**, 29, 1931.

<sup>&</sup>lt;sup>2</sup> Ibid., 23, 213, 1927.

<sup>4</sup> Ibid., 26, 565, 1930.

the iron in solid solution. Since the retarding effect of iron is probably less at 50° and 90° than at 16°,6 the alloys of constant composition obtained at high current densities contain relatively less of this metal at the higher temperatures, and a higher C.D. is required for the constancy to be attained.

The general form of the C.D.-composition curves (Figs. 1 and 2) is the same as that of the curves for the iron-nickel alloys; 2,3 this resemblance applies also to the deposits obtained at 16°.1 In view of the similarity of the deposition potentials of nickel and cobalt 7 and of the influence on them of the simultaneous deposition of iron,8 this resemblance is to be expected. It was pointed out in the previous paper 9 that the retarding effect of iron on the deposition of cobalt is less than



on the deposition of nickel, and so under similar conditions there should be relatively less iron in the iron-cobalt alloys than in the iron-nickel alloys. The results obtained in the present work (see Table I., below) are in agreement with this anticipation.

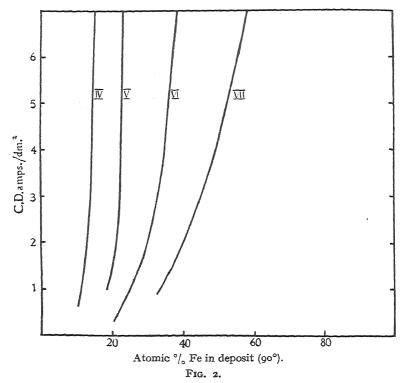
Comparison of Iron-Cobalt, Iron-Nickel and Cobalt-Nickel Alloys. —It is of interest to compare, as was done in Part I. for the results at 16°, the behaviour of the three pairs of alloys falling into the natural order of iron-cobalt, iron-nickel and cobalt-nickel; in each case the firstmentioned metal of a pair (referred to as A) has a similar influence on the deposition of the second metal (B). The compositions of the alloys

<sup>&</sup>lt;sup>6</sup> Ref. 3, page 377. <sup>8</sup> *Ibid.*, 2899, 1926.

<sup>&</sup>lt;sup>7</sup> Glasstone, J. Chem. Soc., 2889, 1926.

<sup>&</sup>lt;sup>9</sup> Ref. 1, page 739.

containing the maximum proportion of A, for the solutions containing 10, 30 and 50 per cent. of the total metal as A, are collected in Table I., for temperatures of 50° and 90°. It will be observed from Fig. 2 that at



90° the maximum content of A—iron in this instance—is only attained at current densities beyond the scope of the present work; the results quoted in the Table may be regarded, however, as being within 2 or 3 per cent. of the true values.

TABLE I.

	Maximum A Per Cent. in Deposit.							
A Per Cent. in Solution.	50°.			90°.				
	Fe—Co.	Fe—Ni.	Co—Ni.	Fe—Co.	Fe—Ni.	Co-Ni.		
10 30 50	18 36 51	39 70 79	51 79 86	15 23 38	<u>—</u> бо	45 75 85		

A comparison of the results, both at  $50^{\circ}$  and at  $90^{\circ}$ , shows the same gradation as was observed at  $16^{\circ}$  and discussed in Part I.

A gradation of another type is found in the "initial" deposits obtained at very low current densities and which contain a minimum

proportion of the component A; the appropriate results are collected in Table II. It should be remembered that the compositions quoted can only be regarded as very approximate, on account of the difficulties of obtaining deposits at the very low current densities, especially at elevated temperatures, capable of being analysed with any degree of accuracy.

TABLE II.

	Minimum A Per Cent. in Deposit.								
A Per Cent. in Solution.	Fe—Co.		Fe—Ni.			Co—Ni.			
	16°.	50°.	90°.	16°.	50°.	90°.	16°.	50°.	90°•
10 30 50	· 9 15 23	7 16 20	8 15 19	11 21 22	6 11 13	 	56 80 90	11  27	2 10 14

It will be observed that whereas an increase of temperature, especially from 16° to 50°, has a very marked effect on the composition of the initial cobalt-nickel deposits, the effect is less with the iron-nickel alloys, and in the iron-cobalt series the compositions of the first deposits, obtained at culowrrent densities, appear to vary only slightly with the temperature.

### Summary.

(I) The variation with C.D. of the compositions of the alloys deposited from buffered solutions containing various proportions of ferrous and cobalt sulphates has been studied at temperatures of 50° and 90°.

(2) The compositions of the alloys tend towards a constant value as the C.D. is increased; this value appears to be independent of the hydrogen

ion concentration of the electrolyte.

(3) A comparison is made of the three series of alloys which fall into the natural order iron-cobalt, iron-nickel and cobalt-nickel; the alloys deposited at both low and high current densities show gradations in properties in harmony with this order.

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# CONDUCTIMETRIC ANALYSIS. I. ACIDS AND ACID MIXTURES.

By Edwin C. Righellato and Cecil W. Davies.

Received 25th November, 1932.

Conductimetric analysis, although possessing a fairly extensive literature, culminating in the systematic researches of Kolthoff <sup>1</sup> does not seem to have had its peculiar advantages widely exploited. This is probably due in part to the lack of apparatus specially designed for

<sup>&</sup>lt;sup>1</sup> Kolthoff, "Konduktometrische Titrationen," Steinkopff, 1923.

the purpose, and partly to a number of minor disabilities and drawbacks which, we believe, can be overcome. The present paper describes an improved form of apparatus, and some modifications of the method in its application to the estimation of acids and acid mixtures.

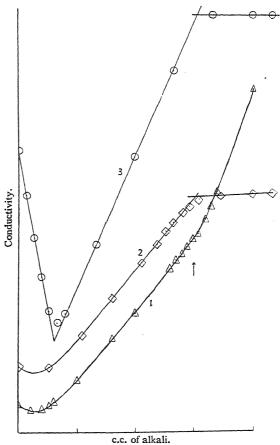
Apparatus.—The usual procedure 2 has been to employ the ordinary conductivity apparatus, consisting of induction coil, telephone, and a Wheatstone bridge network containing a resistance box, cell, and metre bridge wire; the resistance of the cell is given by  $R \cdot x/(1000 - x)$ , where R is the value of the known resistance and x is the bridge wire reading at the null-point. With this arrangement the endpoints can be determined rapidly, but the total time occupied in an estimation is greatly increased by the calculations (which may involve bridge calibration corrections) that are necessary before conductivities can be plotted against amounts of reagent added; a further drawback is that the endpoint in the titration can often not be detected until the subsequent calculations are completed, and many unnecessary readings have been made. To avoid this we have used a form of apparatus in which the resistance of the cell solution is read off directly, and its reciprocal can then be immediately plotted against the amount of reagent added. Our apparatus was improvised from components at hand, and rather than describe this in detail we shall outline the arrangement we recommend, which can readily be built by an instrument maker. The decade resistance box possesses three dials for resistances of the order 10, 100 and 1000 ohms; the unit decade, however, is replaced by a continuous wire of 12 or 15 ohms resistance fitted with a pointer moving over a circular scale graduated in tenths of an ohm. The box also contains two fixed ratio arms of 100 ohms resistance, and is fitted with the necessary terminals for the conductivity cell, source of current (with switch), and telephone. The resistance coils and ratio arms must be non-inductively wound, and the coils must be suitably spaced to avoid stray couplings between the various parts of the bridge. A bridge of this kind is very compact, and rapid and easy to use. In operation, the pointer of the unit dial is put at an intermediate position of, say, 6 ohms, and the other dials are set to the position of minimum sound; a movement of the unit dial then gives the exact resistance of the cell. With this equipment the individual points in the titration curve may be found without effort to an accuracy of 0.1 per cent., and it may be noted that an accuracy of this order is needed in a method of analysis, such as this, of which extrapolation is the essence.

The rest of our equipment consists of a valve oscillator of the Woolcock and Murray-Rust pattern  $^3$  a single telephone earpiece as detector, and, as conductivity cell, a wide-mouthed bottle of 250 c.c.s capacity, the stopper of which carries glass tubes enclosing the leads to the electrodes (blacked platinum discs of about 4 cm². area), and has also an opening through which the reagent is added from a small burette graduated in 0-01 c.c. divisions. During a measurement the cell is almost immersed in a thermostat at  $25 \pm .02^{\circ}$ , where it stands on a shelf which also accommodates the reservoir from which the burette can be replenished. An amplifier of the type described by Hall and Adams  $^4$  has been used in some experiments, and enables the endpoint to be determined in a noisy laboratory with the minimum of effort.

#### Estimation of Acids.

Strong Acids.—The curve for the titration of a highly dissociated acid is well known; the conductivity first falls, through the replacement of hydrogen-ion by the added cation, and then, after the neutralisation point has been reached, rapidly rises with further additions of a strong alkali. The two branches of the curve are straight lines provided the volume of reagent added is negligible, and their intersection gives the

Ιt has endpoint. been usual in the past to assume that the volume change is negligible so long as the reagent is at least ten times as concentrated as the solution titrated; but actually it is easy to show that if the solution is diluted by 10 per cent. during titration (including the excess necessarily added), the apparent endpoint may be as much as 2 per cent. too low. We have therefore applied a " dilution correction" to many of our results, by multiplying each measured conductivity by the ratio: Total volume of solution in cell/ This Initial volume. is not a complete correction, since it ignores the slight mobility changes due to the diffusion of the ionic atmosphere, but it is very nearly so. We have applied the same correction to



The end point is indicated by an arrow.

Fig. 1.

mixtures containing weak electrolytes; here it ignores, in addition, the small change in the degree of dissociation, but it is still a close approximation, and we have found it essential to the correct interpretation of many of the curves for the mixtures studied in the next paper.

Weak Acids.—In the titration of a weak acid with a strong base the conductivity rises from the beginning, as the almost undissociated acid is progressively converted into its salt. When the end-point is passed the conductivity rises more rapidly; the change in slope may not be abrupt owing to hydrolysis, but by extrapolation from the straight portions of the curves the endpoint can be obtained. It has been pointed

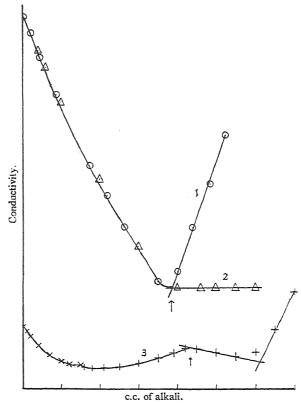
out 5 that a weak acid can also be titrated with a weak base, and, indeed. that in this case the effect of hydrolysis is smaller; but it has not been generally recognised that there are marked advantages in using a weak base, where possible, for the titration of a weak acid, or a mixture containing a weak acid. To confirm this conclusion we have carried out the titration of 100 c.c.s of 0.00292 N-acetic acid with potassium hydroxide and ammonia, and the results are shown in Fig. 1. Curve I shows the titration with 0.0973 N-potassium hydroxide, and Curve 2 with ammonia of the same concentration, and it will be seen that the use of ammonia has several advantages: (I) the endpoint is much more easy to detect, as the titration proceeds; (2) the lines intersect at a more acute angle and the titration is correspondingly more accurate; (3) at dilutions as high as those used here, hydrolysis and the carbon dioxide error prevent the accurate determination of the endpoint when a strong alkali is used. With extremely weak acids it is impossible to determine the endpoint accurately with ammonia, and the use of a strong alkali is preferable.

Moderately Strong Acids.—Neither of the two methods discussed is applicable to acids which are markedly, but not completely, ionised. The term "moderately strong" must necessarily be indefinite, since the dissociation of the acid depends on its concentration as well as its dissociation constant. An illustration is provided by Curve I of Fig. 2, which shows the titration of 200 c.c.s of 0.005 N-nitrobenzoic acid with 0.130 N-potassium hydroxide. The neutralisation line is curved in the neighbourhood of the endpoint, and it is impossible to determine the latter accurately. Kolthoff 6 has studied this problem, and suggests the following method of estimation. After the acid has been titrated as in Fig. 2, Curve I, the cell is refilled with 200 c.c.s of water and successive additions of 0.130 N-potassium nitrobenzoate are made. These results must lie on a straight line which passes through the neutralisation point, and the latter is identified by the intersection of this line with the straight line corresponding to excess of potassium hydroxide in the first titration. This method is of extremely limited applicability, since it involves a knowledge of the nature of the acid being titrated and a supply of the appropriate salt, and moreover any indifferent constituents of the mixture under test, electrolyte or non-electrolyte, must be present at the same concentration during the second titration. We have tested two methods which are more practicable and are of general application. the first, the acid is titrated with ammonia; if the endpoint cannot be determined from this curve with the desired accuracy, a second titration is carried out using potassium hydroxide of the same concentration. The two curves are practically identical up to the neutralisation point, and above this straight lines are obtained in both titrations, the intersection of which fixes the endpoint. The two standard alkalies need not be of exactly the same concentration if the "amounts added" in the two titrations are reduced to a common basis before the results are plotted. If the endpoint is required with great accuracy, a correction should be applied for the fact that the conductivity of the ammonium salt is approximately 0.6 per cent. lower than that of the potassium salt. The process is illustrated in Curves 1 and 2 of Fig. 2.

The second method is neater, in that only one titration is necessary. It consists in adding a small amount of ammonia to the acid and then completing the titration with sodium hydroxide. The method is illus-

trated in Curve 3 of Fig. 2, which shows the titration in this way of 200 c.c.s of 0.005 N-mandelic acid. When the acid has all been neutralised

the conductivity of the mixture falls owing to the replacement ammonium ion the more slowly moving sodium ion; when the displacement of the ammonia is complete the conductivity abruptly rises, and at this endpoint the total amount sodium hydroxide added is equivalent to the originally acid present. Alternatively, the acid present is also measured by the total alkali added up to the point at which the confalls. ductivity This method of titrating with ammonia followed by caustic soda can be used to improve the endpoint in any weak acid titration.



The end points are indicated by arrows.

Fig. 2.—Titration of (1) 0.005 N o-nitrobenzoic acid with 0.130 N KOH; (2) 0.005 N o-nitrobenzoic acid with 0.130 N NH3; (3) 0.005 N mandelic acid with NH3 followed by NaOH.

#### Acid Mixtures.

A Strong and a Weak Acid.—A mixture of a strong and a weak acid can be analysed conductimetrically by means of a single titration? On adding a strong alkali to the mixture the conductivity falls until the strong alkali is neutralised, then rises as the weak acid is converted into its salt, and finally rises more steeply as excess of alkali is added. The three branches of the graph will be straight lines except in so far as (I) increasing dissociation of the weak acid causes a rounding off of the first endpoint, and (2) hydrolysis of the weak salt leads to a rounding off of the second endpoint. Usually, extrapolation of the straight portions of the three branches leads to definite endpoints. Here, again, we consider that ammonia is normally preferable to a strong alkali, for the reasons mentioned in discussing weak acids. Fig. I, Curve 3, illustrates

its use in analysing a mixture of hydrochloric and acetic acids; this may

be compared with Curves I and 2 of Fig. I.

Kolthoff has considered the disturbance arising through increasing ionisation of the weak acid during the first part of the titration. It should be noted however that a further source of error arises from the fact that the weak acid will not be totally undissociated (as the theory of the method demands) at the beginning of the titration. The result of this, as will be clear from the discussion given in the next section, is that the proportion of strong acid found will be too high, and the error

The end points are indicated by arrows.

Fig. 3.—Neutralisation curve for a mixture of hydrochloric and formic acids.

will be the greater the smaller the proportion of the strong acid and the higher the dissociation constant of the weak acid. This error may therefore be imwhen the portant method is used to estimate small proportions of mineral acid present as impurities in weak acids. We suggest that it be avoided by adding a known amount of a acid to mixture before titrating, and determining strong acid originally present by difference; alternatively, methods described in the next section may be applied.

A Strong and a Moderately Strong Acid.—The second acid may be so strong that the neutralisation line is curved throughout, and the two endpoints cannot be found by extrapolation. This is illustrated in Fig. 3, where the circles show the course of neutralisa-

tion by potassium hydroxide of a solution 0.01 N with respect to hydrochloric acid and 0.01 N with respect to formic acid; the curve has been constructed by calculation, using the known mobility values, and  $K=2\times 10^{-4}$  for the dissociation constant of formic acid. Such a mixture has not been satisfactorily treated. Kolthoff 8 employs the following method; after the mixture has been titrated the cell is refilled with an equal volume of water, and the "salt line" constructed by adding to this a potassium chloride solution of the same concentration

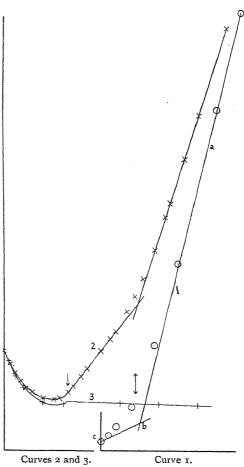
<sup>&</sup>lt;sup>8</sup> Op. cit., p. 32; Z. anorg. Chem., 111, 28, 1920.

as the potassium hydroxide used in the first titration; the intersection of the "salt line" and the neutralisation line is regarded as the endpoint in the titration of the hydrochloric acid. That this cannot be correct will be clear from Fig. 3; the point of intersection gives a result

4 per cent. too high, the reason for this being that the formic acid was 2 per cent. ionised in the original mixture, so that the whole neutralisation line lies above the line for the neutralisation of hydrochloric acid (shown as ab in the figure); it is the latter that necessarily intersects the "salt line" at the true endpoint.

In the particular instance just considered the error is not very great, but this is only due to the fact that formic acid is almost weak enough to be treated as a typically weak acid; this will be evident on drawing a straight line through the points cd in Fig. Actually the method can lead to very large errors. For instance, a calculated curve was constructed, in the same way, for a solution 0.01 N with respect to an acid of dissociation constant  $K = I \times IO^{-3}$ and 0.001 N with respect to hydrochloric acid. Here the "salt line" method gave 40 per cent., instead of 9 per cent. strong acid, the main reason being that the initial conductivity of the solution was more than three times the conductivity of the hydrochloric acid it contained.

Evidently therefore there is need of a new



First end point indicated by downward arrow. Second end point indicated by a double-headed arrow.

Fig. 4.—Curve 1. Titration of neutralised mixture of hydrochloric and mandelic acids with o 926 N HCl (on a different scale from curves 2 and 3).

Curve 2. A mixture of 0.0025 N mandelic acid and 0.0025 N phenol titrated with 0.151 N NaOH.

Curve 3. The same mixture titrated with 0.151 N pyridine.

method of determining the strong acid present in such a mixture, as well as a method of determining the weaker constituent. The only method we have tested involves more than one titration. First, the total acid is determined in one of the ways already described under the heading

"moderately strong acids." The neutralised solution is then titrated with a concentrated solution of a strong acid; this displaces the weaker acid from its salt, and then, if added in large excess, suppresses its ionisation. The slope of the theoretical line for the first process is determined by the difference in mobilities of the strong acid anion and the weaker acid anion. The second part of the conductivity curve must ultimately become rectilinear, and extrapolation then gives the amount of weaker acid present in the mixture. The process is illustrated in Fig. 4, Curve I, which shows experimental results for a solution 0.001 N with respect to hydrochloric acid and 0.005 N with respect to mandelic acid. After determining the total acid present as shown in Fig. 2, the neutralised mixture was titrated with 0.926 N HCl. The straight line ab represents the addition of excess of hydrochloric acid, and bc shows the theoretical curve for the displacement of the weak acid from its salt, drawn from the relation: Slope of ab/Slope of  $bc = (\Lambda_{\text{H}} + \Lambda_{\text{Cl}})/(\Lambda_{\text{Cl}} - \Delta_{\text{Mand}}) =$ (351 + 76)/(76 - 30), where these are the mobilities of the ions concerned at infinite dilution; approximate values are sufficient. The intersection of bc with the straight line drawn through the final points of the titration gives the amount of mandelic acid present.

A Moderately Strong and a Weak Acid.—The treatment of mixtures of this type must depend on the dissociation constants of the two acids. If the stronger acid has a constant of the order  $K = 1 \times 10^{-3}$ the mixture may be converted into one of the previous type by working throughout at high dilutions. If the stronger acid is somewhat weaker than this, we find that an approximate separation of the two can be made by carrying out titrations (I) with a strong alkali, and (2) with pyridine or some other very weak base. With the latter, hydrolysis becomes very marked after the whole of the stronger acid is neutralised, and a comparison of the two curves gives the approximate amount of the stronger acid, while the first gives an accurate value for the total acid. Curves 2 and 3 of Fig. 4 show the titration of a mixture of 0.0025 N mandelic acid and 0.0025 N phenol with 0.15 N sodium hydroxide and 0.15 N pyridine. The curves show the method under the most unfavourable conditions, since the titration curve at the first endpoint happens in this instance to be nearly horizontal, but even so it will be seen that the method makes possible a rapid approximate estimation of both constituents of the mixture.

Two Weak Acids.—This case has been considered by Kolthoff (op. cit.). The separate estimation of both acids is only possible when their dissociation constants, and also the mobilities of their anions, are markedly different.

#### Conclusions.

To propose a general method for the analysis of acids and acid mixtures is impracticable, and the most suitable procedure in any instance must be determined by the concentration and the dissociation constants of the acids. Where the nature of the acid or acids present is known, the considerations advanced should enable a proper choice to be made between the use of a strong or a weak alkali as titrating agent. If, on the other hand, the nature of the solution is quite unknown, we suggest that reliable information as to its acid-base properties is best obtained by titrating samples with a strong base and with a weak base, and also with a strong acid. The same considerations will apply, mutatis mutandis, to the estimation of alkaline solutions.

#### Summary.

A type of apparatus is described which is specially adapted for use in conductimetric analyses, or other rapid conductivity measurements.

Some modifications and additions are proposed to the methods available for estimating acids and acid mixtures.

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# CONDUCTIMETRIC ANALYSIS. II. TAN LIQUORS AND LEATHER EXTRACTS.

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The value of the conductimetric method has not, we believe, been adequately recognised as a means of examining solutions such as extracts of leather, paper, textiles and so on, where the material itself s mainly non-electrolyte, and the electrolyte appears in small quantities (whether as an important constituent, a dangerous contamination, or a valuable indication of previous treatment). To such materials conductivity methods are specially adapted, as they also serve to elucidate the acid-base equilibria which are often of importance in these fields.

The conductivity method presents obvious advantages in that it can be used in coloured or turbid solutions, that it is normally unaffected by any non-electrolyte present and is not subject to interference from electrode processes, and that it retains its accuracy at very high dilutions. In addition, the conductivity method has an outstanding advantage in that both free and combined weak acid (or base) can be accurately estimated, so that a reasonably complete examination of a material as regards its acid-base and buffer properties is possible. Thus, an acid extract may be titrated with alkali to determine (I) the free strong acid, (2) the free weak acid, and (3) the combined weak base; and the combined weak acid can then be found by a second titration using a strong acid as titrating reagent. Finally, the amount of a salt of a strong acid and a strong base may approximately be found, by difference, from the initial conductivity of the extract, and furthermore an idea of the dissociation constants of the weak constituents can be gained from an analysis of the titration curves.

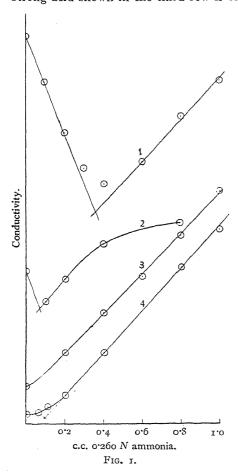
The work reported in this paper was primarily undertaken to test the applicability of the method to the determination of strong acids in leather, a problem which, in spite of its importance, seems to have found no completely satisfactory solution. In addition, some preliminary results are included on other aspects of the examination of leathers.

The Estimation of Strong Acids.—Fig. I shows the titration of four leather extracts with 0.26 N-ammonia. The leathers were extracted with water in a Procter extractor; in Curves I, 3 and 4 the amount taken for analysis corresponded to 2 gm. leather, in Curve 2 to I gm. The curves are typical of a number that have been obtained in this way. Curves 3 and 4 show the leathers concerned to be free from strong acid,

whilst the other two samples clearly contained a strong acid; from the endpoints shown the following figures are calculated:—

	r.	2.	3.	4.
C.cs. o 26 N-ammonia required Weight of leather (gms.) Gequivs. strong acid/gm. leather  p <sub>H</sub> of extract (1 gm. leather/50 c.cs. water	0·36	0·075	nil	nil
	2	I	2	2
	4·7 · 10 - 5	2·0 . IO - 5	nil	nil
	3·03	3·40	> 4	3·98

The first two rows of figures give the data from which the content of strong acid shown in the third row is calculated. For comparison with



experimental  $p_H$  figures this value is then multiplied by 20 to give the hydrogen ion concentration of a I gm./50 c.c. water extract, and the corresponding  $p_{\rm H}$  value is shown in the fourth row. For sample 3, the shape of the curve and its position on the scale of ordinates show that only weakly ionised acids are present and that the  $p_{\mathbf{H}}$  of the extract cannot be less than 4. weak acid present in Sample 4 is stronger (vide infra), and the calculated  $p_{\rm H}$  value is slightly less than 4.

It may be noticed in Curve 2 that the later points in the titration lie off the theoretical straight line. This is attributed to hydrolysis of the ammonium salt formed, and indicates that the leather extract contains one or more extremely weak acids. Similar results have been obtained in a number of titrations, and for further work of this nature we recommend the use of a strong alkali in place of ammonia in order to reduce this disturbing factor.

To confirm our results we have also examined some extracts to which known amounts

of a strong acid had been added. In one experiment, sulphuric acid was added to a tan liquor known to be free from strong acid and buffer salts, so as to give a solution containing 0.000778 g. equivs. per 25 c.c. Subsequent titration gave curves quite similar to Curve 1 of Fig. 1, and the strong acid found in 25 c.c. of a filtered sample was 0.000772 g. equivs., and in 25 c.c. of an unfiltered sample 0.000772.

These and our other results have satisfied us that the conductivity method enables strong acid to be determined accurately in leather extracts and tan liquors. The main limitation of the method has been discussed in the preceding paper: it is impossible to estimate accurately very small amounts of strong acid when accompanied by large amounts of a moderately highly dissociated acid; this set of circumstances does not seem to be often encountered in leather extracts.

Absolute Conductivities.—To check and extend our conclusions, the cell constant of the cell used was determined with dilute potassium chloride solutions and found to be 0·1058. With this information the slopes of the titration curves may be checked from a knowledge of the mobilities. The values used for the latter were:

Ion . . H. 
$$NH_4$$
 K.  $Na$  OH'  $Cl'$   $SO_4$ "  $CH_3CO_2$ ' A' Mobility at 25° 35° 74 74.5 5° 195 75.5 79 41 3°

Here A' represents the organic anion(s) present in the extract, and the mean value, 30, is assumed by analogy with known benzene derivatives

The slope for the neutralisation of a strong acid is now calculated as follows. Addition of I c.c. of f-N alkali leads to the replacement of f. 10<sup>-3</sup> g.-equivs. of hydrogen ion by the cation of the alkali. V is the volume of solution in the cell in c.c.s, the replacement amounts to f. 10  $^{-3}/V$  g.-equivs. per c.c.; the change in the specific conductivity is therefore  $(\Lambda_{\rm H} - \Lambda_{\rm C})$  f. 10<sup>-3</sup>/V ohms<sup>-1</sup> per c.c., where  $\Lambda_{\rm C}$  is the mobility of the cation. Finally, the observed slope of any linear branch of a titration diagram will be  $\Delta\Lambda$  . f/1000 C . V, where  $\Delta\Lambda$  is the mobility change, and  $\mathcal C$  the cell constant. This formula is applicable to values corrected for dilution (v. Part I.); we have not applied corrections for interionic forces to the mobility values, since the solutions we have used have all been very dilute. The straight lines drawn in Figures 1 and 2 have all been drawn with these slopes, and it will be seen that the theoretical treatment can sometimes assist greatly in interpreting results, as in Fig. 1, Curve 2, where hydrolysis makes the correct extrapolation of the second branch of the curve from the measurements themselves a matter of some doubt. It is often claimed as an advantage of conductivity methods that absolute measurements are unnecessary; but a cell constant determination takes little time, and it is well worth while not to neglect the aid afforded by the theoretical interpretation in determining endpoints, and in avoiding errors. Failing a separate cell constant determination, a diagram should at least be constructed for the neutralisation of a standard acid by alkali, and the theoretical slopes for other reactions calculated from this and the known mobility changes.

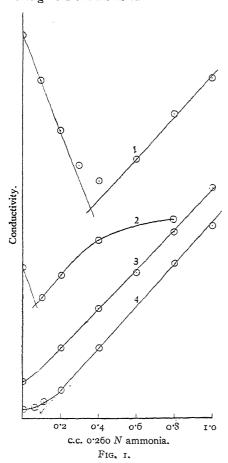
Complete Analysis of a Leather Extract.—In two instances we have attempted a more or less complete analysis of a leather extract as regards its acid-base properties, and a description of this work will indicate the information that can be gained.

The first was an extract of a leather tanned with sumac alone. Titration of this with ammonia and with potassium hydroxide showed the extract to be free from strong acid; further, the satisfactory concordance, after allowing for hydrolysis, between the two results showed that addition of strong alkali did not displace any weak base from combination in the extract. The mean of the two titrations gave 0·106 g.-equivs. as the amount of free weak acid per 100 gm. leather extracted, and that this acid is extremely weak will be seen from Curve 3 of Fig. 1, which illus-

whilst the other	two	samples clearly contained a strong acid	from the
endpoints shown	the	following figures are calculated:—	

	r.	2.	3.	4.
C.cs. 0-26 N-ammonia required Weight of leather (gms.) Gequivs. strong acid/gm. leather $p_{\rm H}$ of extract (1 gm. leather/50 c.cs. water	0·36	0.075	nil	nil
	2	I	2	2
	4·7·10 - 5	2.0.10 - 5	nil	nil
	3·03	3.40	> 4	3·98

The first two rows of figures give the data from which the content of strong acid shown in the third row is calculated. For comparison with



experimental  $p_{\rm H}$  figures this value is then multiplied by 20 to give the hydrogen ion concentration of a 1 gm./50 c.c. water extract, and the corresponding  $p_{\mathbf{H}}$  value is shown in the fourth row. For sample 3, the shape of the curve and its position on the scale of ordinates show that only weakly ionised acids are present and that the  $p_H$  of the extract cannot be less than 4. weak acid present in Sample 4 is stronger (vide infra), and the calculated  $p_{\mathbf{H}}$  value is slightly less than 4.

It may be noticed in Curve 2 that the later points in the titration lie off the theoretical straight line. This is attributed to hydrolysis of the ammonium salt formed, and indicates that the leather extract contains one or more extremely weak acids. Similar results have been obtained in a number of titrations, and for further work of this nature we recommend the use of a strong alkali in place of ammonia in order to reduce this disturbing factor.

To confirm our results we have also examined some extracts to which known amounts

of a strong acid had been added. In one experiment, sulphuric acid was added to a tan liquor known to be free from strong acid and buffer salts, so as to give a solution containing 0.000778 g.-equivs. per 25 c.c. Subsequent titration gave curves quite similar to Curve I of Fig. I, and the strong acid found in 25 c.c. of a filtered sample was 0.000772 g.-equivs., and in 25 c.c. of an unfiltered sample 0.000772.

These and our other results have satisfied us that the conductivity method enables strong acid to be determined accurately in leather extracts and tan liquors. The main limitation of the method has been discussed in the preceding paper: it is impossible to estimate accurately very small amounts of strong acid when accompanied by large amounts of a moderately highly dissociated acid; this set of circumstances does not seem to be often encountered in leather extracts.

Absolute Conductivities.—To check and extend our conclusions, the cell constant of the cell used was determined with dilute potassium chloride solutions and found to be 0.1058. With this information the slopes of the titration curves may be checked from a knowledge of the mobilities. The values used for the latter were:

Ion . . . H. 
$$NH_4$$
 K.  $Na$  OH' Cl'  $SO_4$ "  $CH_3CO_2$ ′ A' Mobility at 25° 350 74 74.5 50 195 75.5 79 41 30

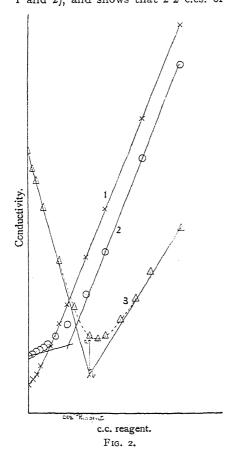
Here A' represents the organic anion(s) present in the extract, and the inean value, 30, is assumed by analogy with known benzene derivatives at 25°.

The slope for the neutralisation of a strong acid is now calculated as follows. Addition of I c.c. of f-N alkali leads to the replacement of f. 10 - 3 g.-equivs. of hydrogen ion by the cation of the alkali. V is the volume of solution in the cell in c.c.s, the replacement amounts to f. 10  $^{-3}/V$  g.-equivs. per c.c.; the change in the specific conductivity is therefore  $(\Lambda_{\rm H^{-}} - \Lambda_{\rm C^{+}}) f$ . 10<sup>-3</sup>/V ohms<sup>-1</sup> per c.c., where  $\Lambda_{\rm C^{+}}$  is the mobility of the cation. Finally, the observed slope of any linear branch of a titration diagram will be  $\Delta\Lambda$  . f/1000 C . V, where  $\Delta\Lambda$  is the mobility change, and  $\mathcal C$  the cell constant. This formula is applicable to values corrected for dilution (v. Part I.); we have not applied corrections for interionic forces to the mobility values, since the solutions we have used have all been very dilute. The straight lines drawn in Figures 1 and 2 have all been drawn with these slopes, and it will be seen that the theoretical treatment can sometimes assist greatly in interpreting results, as in Fig. 1, Curve 2, where hydrolysis makes the correct extrapolation of the second branch of the curve from the measurements themselves a matter of some doubt. It is often claimed as an advantage of conductivity methods that absolute measurements are unnecessary; but a cell constant determination takes little time, and it is well worth while not to neglect the aid afforded by the theoretical interpretation in determining endpoints, and in avoiding errors. Failing a separate cell constant determination, a diagram should at least be constructed for the neutralisation of a standard acid by alkali, and the theoretical slopes for other reactions calculated from this and the known mobility changes.

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trates the first part of the titration with ammonia, and exhibits practically no initial "kink" due to ionisation of the free acid. Titration of the extract with sulphuric acid (Fig. 2, Curve 2) shows that a weak acid is displaced from combination by the strong acid added (cf. Fig. 4, Curve 1, of preceding paper). To determine the amount of this buffer salt more accurately, an excess of sulphuric acid was added to the extract, and the solution back-titrated with potassium hydroxide. The result is illustrated in Fig. 2, Curve 3 (on a different scale from Curves I and 2), and shows that 2·2 c.cs. of 0·1 N-acid are used in displacing



the combined weak acid from 2 grams of leather; this agrees with the result of Curve 2 of Fig. 2, and shows the presence of OOII g.-equivs. of combined weak acid per 100 gm. leather. It will be noticed from Curve 3 that the liberated acid has a far higher dissociation constant than the acid or acids originally in the free state in the extract; even allowing for the "common ion" effect the behaviour of the extract cannot be reconciled with the presence of a single, partly neutralised, acid. length ab in Fig. 2 represents the conductivity of the liberated acid, and since its concentration is known its dissociation constant can be approximately calculated. The data plotted in the figure are for an extract of 2 gm. of leather in a total volume of 160 c.cs., so that the concentration of the acid is  $(0.011 \times 1000)/(50 \times 160) =$ 0.00138 g.-equivs. per whilst its specific conductivity is  $2 \cdot I \times IO^{-4}$ ; hence its equivalent conductivity is 152. Assuming its conductivity at infinite dilution to be 350 + 30 =380, the application of Ostwald's dilution formula,  $\Lambda^2$  .  $C/\Lambda_0(\Lambda_0$  —

 $\Lambda)=K$ , gives  $3.7 \times 10^{-4}$  as the dissociation constant of the acid. From the nature of the calculation this result can only be approximate; a second calculation, based on the  $p_{\rm H}$  of an extract to which some sulphuric acid had been added, gave  $5.1 \times 10^{-4}$  for the dissociation constant. From the order of magnitude of the constant it may be suspected that the acid is a hydroxybenzoic acid. The free acid in the extract is very much weaker, and may be phenolic in character.

Finally, some further information can be gleaned from the initial conductivity of the extract. For different extracts of 2 gms. of the leather in 150 c.c.s, the specific conductivity was  $3.00 \times 10^{-4}$ ,  $3.28 \times 10^{-4}$ , and  $3.21 \times 10^{-4}$ ; mean,  $3.16 \times 10^{-4}$ . This is too large to be attri-

buted to the free acid, which can be seen from Curve 3 of Fig. I not to contribute materially to the conductivity, and to the salt of the combined weak acid. Assuming the equivalent conductivity of the latter to be approximately 100, its specific conductivity should be I·55 × 10<sup>-4</sup>; the remainder, I·61 × 10<sup>-4</sup>, must be attributed to an electrolyte that does not enter into any of the reactions studied, that is, to the salt of a strong acid and a strong base, and this must also be present at a concentration of approximately 0·01 g.-equivs. per 100 gms. of leather.

A similar study of extracts of a second leather that had been tanned

A similar study of extracts of a second leather that had been tanned with mimosa gives results in marked contrast with those just described. Titration with ammonia and potassium hydroxide show, as before, the absence of strong acid and of weak cations, and give 0.055 g. equivs. as the content of free weak acid per 100 gms. leather. Curve 4 of Fig. 1 shows the first part of this titration with alkali, and it will be seen that there is an initial kink in the curve which has no counterpart in the other leather studied (Curve 3). This is due to the ionisation of the weak acid in the extract, and on extrapolating the line for salt formation back to the point for zero addition the conductivity due to the acid is found, and its apparent dissociation constant can be calculated as before. This gives the value  $K = 2 \times 10^{-6}$ ; here, however, it is assumed that the extract contains only one acid, and the results are also open to the interpretation that there is present a small amount of an acid of higher dissociation constant together with a large proportion of a much weaker acid.

The titration of this extract with strong acid is illustrated in Curve I of Fig. 2. There is the same initial kink, due in this instance to the suppression of the ionisation of the weak acid present, but no indication of the presence of buffer salts. The whole initial conductivity of this extract, apart from the portion already attributed to the free acid, must therefore be ascribed to inert salts, and the approximate concentration of these is found in the same way as before to be 0.006 g.-equivs. per IOO g.-leather.

The results, per 100 g.-leather, are therefore as follows:-

Leather tanned with Strong acid Free weak acid (gequivs.) Free weak acid: Mean K. Combined weak acid (gequivs.) Combined weak acid: Mean K. Combined weak base Salt of strong acid and strong base	Sumac nil 0.106 < 10 - 7 0.011 4 × 10 - 4 nil 0.01	Mimosa.  nil  0.055 2 × 10 - 6  nil  nil  nil  0.006
--	--	--

Possibly these preliminary results with the materials of the leather chemist may serve to suggest some uses of the method in parallel directions. We wish to express our gratitude to Mr. R. Faraday Innes and other members of the British Leather Research Association for the provision of leathers and extracts, and our appreciation of their interest in the progress of the work.

#### Summary.

Conductivity titrations with leather extracts and tan liquors are used to estimate the amounts present of strong acid, free weak acid, combined weak acid and other constituents.

Battersea Polytechnic, London, S.W. 11.

# REVIEWS OF BOOKS.

Lehrbuch der Physikalischen Chemie. By Dr. KARL JELLINEK, Professor in the Technischen Hochschüle, Danzig. (Stuttgart: Ferdinand Enke. Vol. I. Pp. liii + 966 with 337 diagrams. Price 73.80 RM. unbound. Vol. II. Pp. xiv + 924 with 384 diagrams. Price 79.20 RM. unbound. Vol. III. Pp. xiv + 893 with 240 diagrams. Price 82.80 RM. unbound. Vol. IV. Pp. 624 with 168 diagrams. Price 56 RM. Price of these volumes if the five volumes are ordered is 262.1 RM.).

It is the aim of the author in writing this textbook to build a bridge between physics and chemistry, and although his programme of work is not yet complete, he has already devoted some 3500 pages to this purpose.

Physical chemistry is composed of numerous bridges spanning the unknown between physics and chemistry. These bridges have been built in accord with guiding principles which change from one generation to another; thus the laws of mechanics, the kinetic theory, the electromagnetic theory, thermodynamics, statistical mechanics, quantum mechanics, etc., have all in their turn contributed to the linking up of the two subjects. The unknown territory is being so rapidly built over and the gaps have so far disappeared that it is now uncertain where chemistry ends and physics begins.

The correlation of all of the knowledge gained by the application to chemistry of the constantly changing physical theories is a task of no mean order. The researchers of one generation have not felt it incumbent on them to correlate with any degree of completeness their work with that of their predecessors. This work generally falls to the writers of the scientific textbooks, and when the treatment is as comprehensive as in the present volumes, a very great depth of knowledge is required by the author. Professor Jellinek had special cause to be aware of this fact, for after the completion of the first two volumes of his textbook in 1913-14 he found that his knowledge was insufficient to proceed with the third volume as he originally intended. It was necessary to devote years to the study of the non-euclidian geometry, etc., before he could proceed with the next stage of his programme.

The book reminds one of the famous textbooks of physics and chemistry of the past. It particularly resembles Chwolson's textbook of physics, especially in the manner in which experiment and theory are welded into a complete whole. More than a thousand diagrams are included in the book, of which a large proportion consist of drawings of apparatus to illustrate physico-chemical experimental technique. This insistence on technique is a feature rarely met with in textbooks on physical chemistry. The author has had the benefit of the earlier constructive work of Ostwald, Nernst, and G. N. Lewis, and the mode of treatment of physical chemistry in the present volumes is to a considerable extent based on that of these writers. The textbook, however, differs from those of these physical chemists particularly in respect to the emphasis laid on the kinetic point of view and on the detailed treatment of the mathematical basis of chemistry. Wherever possible both the thermodynamic and the kinetic view-point are given. In the early sections, the two aspects are treated separately, but later on they are employed side by side to give a clearer sense of perspective. The proofs of the numerous theorems are given very fully with a minimum of missing steps in their derivation.

Following an introduction on the fundamental principles of physical chemistry. which includes thermodynamics, about 1400 pages are devoted to the laws governing the existence and physical properties of the three states of aggregation of matter in the pure state. The electrical and magnetic properties are not included at this stage. The basic laws are those of thermodynamics and statistical mechanics, with the introduction of the quantum theory where it is required, particularly to explain the thermal properties of solids. The crystallographic section and the whole of the treatment of the solid state are particularly valuable. The second volume is completed by a section in which the properties of dilute gaseous, liquid, and solid mixtures are treated in the same way as the sections on pure substances. These two volumes differ very considerably from those of the first edition, having been rearranged and very largely rewritten. In the third volume, equilibria in gaseous systems at moderate pressures and in dilute solutions are examined mainly from the thermodynamical point of view. The section on electrochemistry commences in this volume and is expanded in the first parts of Volume IV. The author then attacks the problems of concentrated mixtures, dealing with gaseous mixtures at high pressures and with concentrated liquid mixtures. Solid mixtures are to be treated in the next section of the volume. The bearing of the relativity theory, radioactivity, corpuscular rays, on physical chemical theory will be dealt with subsequently, and later the whole of the newer researches on the electrical constitution of atoms, on spectra, photochemistry, the formation of molecules, and crystal formation, will be incorporated into the material of a final volume.

The volumes already completed show that the work is of first class importance and it will be regarded as one of the classical textbooks of physical chemistry which will be invaluable as a work of reference.

W. E. G.

Liesegang Rings and other Periodic Structures. By Dr. Ernest S. Hedges. (London: Chapman & Hall, Ltd., 1932. Pp. viii + 122 + 8 plates 10s. 6d. net.)

This work gives a very complete account of a phenomenon which has received a good deal of attention, owing partly to its striking character and the ease with which it can be produced in a number of selected cases, and partly, no doubt, to sanguine expectations that it would provide a model or explanation of natural periodic structures. It also provided Wilhelm Ostwald with the only known instance of the "metastable supersaturation" postulated by him, and led him to formulate the first theory of periodic precipitation. This, and later theories advanced by S. C. Bradford, M. H. Fischer, R. Fricke, N. R. Dhar and A. C. Chatterji and, finally, Wolfgang Ostwald are fully stated and discussed. The last named is probably the most satisfactory explanation of periodic precipitation so far advanced and, stated simply, amounts to this: precipitation is inhibited when the other soluble reaction product exceeds a certain concentration and begins again when this has been reduced sufficiently by its diffusing away in both directions. Ostwald in his first papers somewhat obscured matters by talking of three "diffusion waves" (viz. of the two reaction components and the soluble reaction product) and the possibility of their "interference," which is perhaps pushing metaphor beyond its legitimate limits. Dr. Hedges makes great play with the diffusion waves, quoting a number of instances in which there is no third diffusion wave; some of these, however, like the periodic salting out of NaCl by HCl, are not Liesegang rings and therefore beside the point. His

general conclusion is that the effects of the soluble reaction product "cannot be regarded as the fundamental cause of the formation of periodic structures, but rather as one of the most important modifying influences."

The author propounds a "comprehensive theory of periodic structures" which, to quote his own summary statement, requires "(1) a critical condition which has to be reached before crystallisation, precipitation, coagulation, condensation, or other change involved in the formation of the periodic structure takes place, and (2) mobilisation of the material which can occur during the delay caused by the first condition. In this way the material is moved from the zones which eventually become the 'spaces' to those which eventually become the 'rings.'"

Whether the reader will be prepared to call so general a statement a "theory" will depend on his definition of that elastic term; it will hardly tell him whether a given pair of reactants within given limits of concentrations will produce stratifications, information which it is perhaps not unreasonable to expect from a comprehensive theory.

The author devotes brief chapters to other periodic phenomena, such as periodic sedimentation and crystallisation, and to periodic structures occurring in nature, many of which, like the "crimp" in wool, are of considerable interest. Not the least valuable feature of the book is the bibliography comprising no less than 482 references, which bears eloquent testimony both to the amount of attention the Liesegang phenomenon has received in a comparatively short space of time and to the author's knowledge of the literature.

E. H.

Biographical Fragments. By SIR ARTHUR SCHUSTER, F.R.S. (London: Macmillan & Co., Ltd., 1932. Pp. xiii and 268. Price 10s. 6d. net.)

These autobiographical fragments give a delightful picture of education in the sixties and seventies of last century in Germany and of life mainly in this country thereafter. Sir Arthur's account of the Siamese Eclipse Expedition under his charge in 1875 and his walking tour thereafter in the Himalayas is well worth reading not only for its indication of the difficulties of the times (for the first time spectrophotographs of the corona were taken—and dry plates were not invented!) but also for the purely descriptive interest of conditions in the countries visited.

The last sixty pages provide a truly remarkable link with early Victorian science. The author as a distinguished man of science was brought into contact with men of note who will be mere names to the majority of his readers; for nstance, Wöhler (born in 1800), Joule, Kirchhoff, Bunsen, Helmholtz, Hertz. Some of his readers may be able to say that they too have met such men, but there can be few who have had the intellectual joy of scientific comradeship with the heroes of this bygone age.

ABERDEEN: THE UNIVERSITY PRESS

# STUDIES ON ADSORPTION. PART I. MECHAN-ISM OF THE ACTIVATION OF CHARCOAL.

By L. J. Burrage.

Received 23rd November, 1932.

During the past few years a number of papers have been published on the subject of the mechanism of the activation of charcoal. In almost all, however, there was not the slightest information concerning the actual mechanism, but only a detailed examination of the final product

from some definite view point.

It was with the object of investigating the mechanism of activation that the present work was undertaken. The problem has been attacked from two sides, firstly, the botanical and secondly, the chemical. The first of these dealt with the morphological structure, before and after charring, and before and after activation. The generally accepted theory at the moment is that activation consists in a removal, or prevention of the formation, of complex hydrocarbons which poison the active points on the charcoal surface, thereby rendering it inactive. In air and steam activation these bodies are oxidised away, while in the case of chemical activation the strong dehydrating nature of the agents employed prevents the formation of the hydrocarbons.

In the author's view, this latter idea rests entirely on a misconception which has arisen because the earliest chemical activating agents, such as phosphoric acid and zinc chloride, were powerful dehydrating agents. The point which has been entirely overlooked, however, is that these substances are solvents for cellulose, and the new theory is built on this foundation. It affords an explanation of the mechanism of activation,

whether the process employed be air, steam or chemical.

Recently Diesenhammer 1 has published a paper which shows that he is working on similar lines to the author and suggests that activation is due to a dissolving of the cellulose, but this is not specific enough and certainly does not attempt to draw a picture of the resultant surface of the charcoal. As a result of the hypothesis advanced in the present paper, the author has endeavoured to draw a picture indicating to some extent the nature of the charcoal surface, and this representation is in close agreement with the experimental results so far obtained.

It has already been stated that the new theory is partly based on botanical grounds, and it will be advantageous to consider this aspect first. An examination of the structure of wood shows it to be composed almost entirely of cells of various types known as vessels or tracheids. In the course of growth these undergo secondary thickening of the wall, small pores, known as pits, being left to establish connection with neighbouring vessels. These are of various types, each of which is very distinctive.

Fig. 1 (a) represents four tracheids from the pine, the type of pitting being known as bordered pits. This is one of the largest forms of pitting and is very regular. The whole of the cell wall is thickened up to the outside of the two concentric rings. The centre button is also thickened

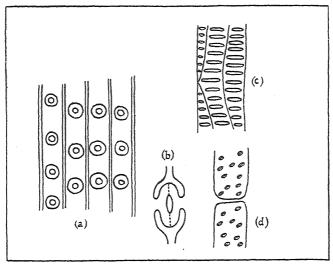


Fig. 1.

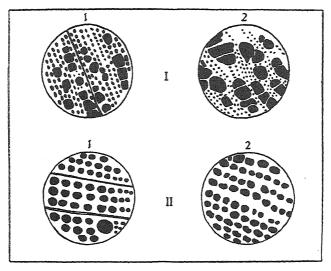
and attached to the wall of the cell by a thin lamella of cellulose. Fig. I (b) represents a bordered pit in cross-section and shows the cell wall with the thickened button and its attachment. Fig. I (c) is an example of scalariform thickening in which the pits are elongated transversely, and Fig. I (d) shows portions of two vessels with another type of pitting on the walls, which is not so regular as in the other cases.

## Examination of the Charcoals with a View to Ascertaining the Nature of the Starting Material.

Some fifty charcoals were examined microscopically and it was found that the original morphological structure of the plant persisted, whatever had been the method of activation, providing that the material had not been crushed during the making of the charcoal (Fig. 2). This structure was found to be quite unaffected by the subsequent evacuation of the charcoal, whether this was carried out at 110°, 270° or 800° C. It was thus a simple matter to state of what general type was the plant from which the charcoal had been made. It was found, however, that one could be much more specific than this. If one powdered the charcoal as finely as possible and examined it under a very high magnification, on a few of the particles one could identify the pitting on the walls of the vessels of the original plant. These pores are peculiar to each particular variety and thus provide a suitable means for the identification of the original substance. It has also a further advantage in that the starting material can be identified even if it has been powdered during the course of its manufacture.

All soft and hardwood charcoals are easily differentiated in this manner. Nut shell charcoals, however, are too similar in appearance to allow of classification by these means, but by a careful scrutiny of the granules one can usually find portions of shell large enough to identify the original nut. With peat the structure is very simple and does not readily allow of identification in the charcoal. All peats, however, contain diatoms and after ashing these may be readily identified.

In the young cell the walls consist of almost pure cellulose, but as the cell grows older, the walls may become permeated with what are known as encrusting substances, the process being known as lignification. This change takes place at the expense of the cellulose and new substances such as lignocellulose are produced. The extreme limit of this change is the production of wood, which contains only about 60 per cent. of cellulose, while lignocelluloses are still considered to contain about 70-80 per cent. of cellulose.



- Soft wood.
   Wood.
- Pine wood.
   Charcoal.

Fig. 2.—Transverse sections.

The present theory of activation is that it is this cellulose, or the charcoal formed from it, which is being acted upon during the activation, whether this be carried out, before, during or after carbonisation, whereas the lignin or the resultant charcoal is untouched. This would cause pitting and it is believed that it is this which activates the charcoal. Assuming this hypothesis to be correct, let us examine the alteration of the adsorption isothermal of a typical non-polar vapour, such as C Cl<sub>4</sub>, with varying degrees of activation of the charcoal. Considering the lower pressure region of the isothermal, in practice, below 0.1 mm. pressure, unactivated charcoal would adsorb practically no vapour, since it has already been postulated that a typically non-polar vapour of this type can only be adsorbed at the active centres, hence the quantity of vapour taken up below 0.1 mm. can only be held by Van der Waals' forces. A slight amount of pitting of the charcoal obtained from the

cellulose causes a corresponding amount of vapour to be adsorbed and so on with increasing activation. It is considered that the active points are the carbonised remnants of cellulose attached to the walls of these activation pores. With continued activation a stage will be reached when there will be no more cellulose charcoal or cellulose to be pitted, and it will merely result in a gradual removal of the activation spikes. This will cause a falling off in the quantity adsorbed below 0.1 mm. pressure since some of the vapour was originally held by the free valencies of the spikes which have now been removed. On the other hand the amount taken up at saturation may increase since there is more space in which vapour may condense between the remaining spikes. This will be dealt with more fully later.

If it is correct that it is the pitting of the cellulose or the resultant charcoal which regulates the capacity of the charcoal for adsorption, then, it is obvious that there are two important factors: (I) The method of preliminary treatment and (2) Activation, which may precede (I) or be carried out either simultaneously or afterwards.

#### Various Methods of Activation.

## A. Air Activation.

This will most certainly give rise to a charcoal which is poor at low pressures and may also be poor at high pressures, according to one of two possibilities:—

(I) This type of activation may give rise to a drastic pitting of the cellulose, thereby making large activation pores which would cause the charcoal to be poor at low pressures, although it might be good at higher pressures; or

(2) That air, being a drastic form of activation, burns away the wood charcoal with such rapidity that only an infinitely small space of time would separate the burning away of the charcoal formed from the cellulose and the charcoal formed from the lignin. This would leave a film of inorganic material which would tend to protect the surface from further activation. Hence the final product would be dusty and have very few activation pores and so behave as a poor adsorbent at both high and low pressures, being, in fact, underactivated.

#### B. Steam Activation.

Steam would be a much milder oxidising agent than air, and would first attack the charcoal formed from the cellulose, thus causing pitting. The charcoal formed from the lignin would not be so readily attacked as in the previous method, since it is more dense than the cellulose charcoal and a milder oxidising agent is being used. This would give rise to a much more active charcoal than in the previous case.

#### C. Chemical Activation.

Most chemical activating agents (all those commonly used) leave inorganic material which is bound to poison some of the active points as well as fill some of the fine activation pores, both of which would markedly affect the capacity of the charcoal at low pressures.

It would be advisable at this point to examine the type of adsorption one would expect to result from a charcoal which has been chemically activated, in the light of the new hypothesis: that chemical activating agents are actually dissolving the cellulose and leaving the lignin.

Let us consider, first, the various agents, all of which are solvents for

cellulose and not for lignin.

Zinc Chloride.—Cellulose readily dissolves in an aqueous solution of this salt on warming while zinc chloride in conc. HCl dissolves cellulose rapidly in the cold. From this it would appear that when cellulose is rapidly dissolved it is a simple matter for the resultant charcoal to be overactivated. Practically the entire cellulose would have been dissolved, giving rise to a charcoal which is very poor at low pressures and very good at high. This is also the effect of poisoning of the active centres by inorganic material, as has already been mentioned, which makes the charcoal still worse at low pressures.

**Phosphoric Acid.**—This is also a well-known activation agent, but so far as could be ascertained there were no data available to show whether this was a solvent for cellulose. Experiments carried out by the author.

however, show that cellulose is readily dissolved.

Action of Ferments.—Marsh gas is formed by ferments in the decomposition of cellulose. This is observed when vegetable matter is undergoing slow decomposition in stagnant water. This type of process must have occurred in peat and, therefore, if this were carbonised and no activation carried out it should show a certain degree of activation due to the action of ferments. It is a reasonable conclusion that at any rate in the early stages the cellulose is acted upon under these conditions, whereas the lignin is untouched, since one is quite familiar with the sight of fallen leaves which have partially decayed leaving a network of veins, which is the hard portion or lignified tissue.

## Starting Materials.

**1. Soft Wood.**—As has already been stated soft woods are very readily attacked by activation agents. The action of air on soft wood charcoals would be too drastic to be efficient, whereas the action of steam should give much better results.

2. Nut Shell.—Since this is a harder material it would be more resistant to air activation than soft wood and therefore give better results. Nut shell charcoal subjected to steam activation would un-

doubtedly give the better results.

3. Peat.—This forms an excellent starting material for chemical activation. It is characterised by the presence of diatoms—siliceous alge—which abound when vegetable matter is undergoing decomposition. Peat should give rise to a fairly good charcoal without activation, as, it is already in a state of partial decomposition, *i.e.*, the cellulose has been partly dissolved by bacterial action, which will give rise to active points on charring. Owing to its simple morphological structure peat has very little lignin and hence is very readily attacked by activation agents. As a result of these two factors one would expect the resultant peat charcoal to be overactivated.

## Possible Explanation of Adsorption Phenomena.

To return to the chemical aspect of this problem, Debye and Scherrer <sup>2</sup> concluded that amorphous carbon was merely graphite in a powder

form. [X-ray examination.] This view was criticised by Ruff, Schmidt and Olbrich, who consider that amorphous carbon is a true modification. From their investigation it would appear that the adsorptive powers of charcoal are due to the amorphous form alone.

The most probable structure of the latter, in view of its mode of formation from cellulose or sugars is that of an interlocking network of carbon chains, which are the degradation products of the original cellulose

molecules.

It has already been stated that lignin contains 50-60 per cent. carbon as compared with 44 per cent. in cellulose, and that it would appear to be more resistant to the attack of solvents and oxidising agents. It does not appear to be a great step to connect graphite in charcoal with the original lignin and the amorphous carbon with the original cellulose. The last fact has been agreed by previous workers. Since lignin has a larger proportion of carbon atoms than cellulose and is more resistant to attack, it follows that in carbonisation, the carbon produced by the lignin may be more dense than that produced from cellulose and again more resistant to attack. The valencies of the large number of carbon atoms packed in a small space will link up and so the attractive force for anchoring molecules on the surface will not be very great.

Now consider the cellulose, or the charcoal produced from the cellulose, in the original plant. This is readily attacked during activation and holes are produced, from molecular size upwards. Since the original plant structure is unaltered by activation, as has been previously mentioned, it follows that the activation pores must be definitely smaller

than the original morphological pores.

It would be as well at this point to give a diagrammatic idea of the various stages of activation and explain the change of low (up to 0.1 mm.) and high (above 0·1 mm.) pressure isothermals in detail with increasing activation of the charcoal in the case of a vapour such as C Cl4. It has been found in practice that isothermals of vapour, such as C Cl<sub>4</sub>, on activated charcoal are curved up to a pressure of O·I mm., but consist of a series of rectangular steps above this pressure. The quantity adsorbed at 0.1 mm, is usually greatly in excess of that adsorbed on the first step. As a working hypothesis it has been assumed in previous publications that each step corresponded to the completion of one ring of molecules round all the available active points. It does not follow that each of the latter will have the same number of rings round it at any given pressure since they do not all possess the same adsorption potential. This applies to those atoms possessing unsaturated primary It is this force which is considered to have the power of developing a sufficiently high field to polarise normally apolar molecules, and thus cause them to be adsorbed. The molecules next to the active centre are practically chemically held, and those in each successive ring have a progressively increased amplitude of vibration, so that the outermost ring will be practically gaseous. In this manner pools of liquid will be formed round each active point.

Apart from those atoms situated in the activation pores, the outermost carbon atoms over the whole surface have at least one free valency, and it is suggested that the molecules which combine in a quasi chemical manner with these carbon atoms, and those which combine with the free valencies of the active centres, comprise the quantity adsorbed up to 0·I mm. If the dipole moment of the molecule is not large, then, beyond this stage adsorption will only occur at highly active centres, and will therefore be limited to the activation pores, with the formation of "pools" or columns of liquid.

On the basis of this hypothesis one is able to give a picture as to the probable nature of the surface of the charcoal itself (Figs. 3 and 4).

In Fig. 3 (a) the surface A is presumed to be the charcoal derived from the original lignin and the surface B the activation pore or capillary formed by the pitting of the original cellulose. Fig. 3 (b) represents a section through this surface A. Here the surface carbon atoms have one free valency which is capable of anchoring a vapour molecule (represented as solid circles). In Fig. 4 a section is shown of the surface of an activa-

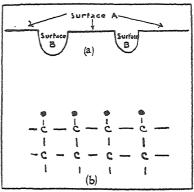


FIG. 3.

tion pore or capillary. In this it will be noted that there are some carbon atoms which function in exactly the same way as at the surface A, whereas others have two or more free valencies and are in chains. These latter are presumed to be the active points. As in the previous case these atoms can anchor a molecule with each free valency, these being represented as solid circles. As has been already mentioned, the quantity of vapour adsorbed at surface A and B under these conditions constitutes the adsorption up to 0·1 mm. pressure. At higher pressures of vapour there will be capillary condensation between the activation spikes giving rise to pools or columns of liquid (shaded portion). The whole of the adsorption above 0·1 mm. pressure is believed to be of this type. Suppose the vapour which is being adsorbed has a large

FIG. 4.

molecule, then, when the surface layer is complete, i.e., when all the primary valencies of the carbon atoms have a vapour molecule attached, there will be practically no room for capillary condensation to occur, hence the isothermal would rise almost vertically from O·I mm. Again, under these conditions one

would expect  $C_XO_Y$  to exert a large poisoning effect, since all the  $C_XO_Y$  sponge must be removed from the active centres before adsorption can take place. Hence activation pores which are not readily accessible will retain their  $C_XO_Y$  and no vapour will be adsorbed. On the other hand a slight increase of the charging pressure of the vapour

will give rise to a large cleaning-up effect, resulting in a greatly increased quantity value at 0.1 mm. on the isothermal. This has actually been achieved.4 Charcoal B 5 was charged with amyl alcohol to saturation at 0.8 mm., the quantity value at 0.26 mm. being 133.0 mgs./gm. recharging to 3 mm. the quantity value at 0.26 mm. was 396 mgs./gm., a great increase in the quantity adsorbed for a somewhat slight increase of charging pressure: Treble the quantity adsorbed at treble the charging pressure. In each case the isothermals rose almost vertically after 0.1 mm. parallel to the pressure axis. Allmand and Chaplin 6 found that the heat of sorption of C Cl4 on charcoal changed suddenly at approximately 0.1 mm., giving rise to a much lower value above this pressure. This is in complete agreement with the present hypothesis, for below 0.1 mm. the vapour is quasi chemically held giving rise to a high heat value while above that pressure, it condenses in the capillaries giving rise to a value of the heat of sorption which approximates to that of the latent heat. It must be greater than this, however, since some of the molecules are quasi chemically held above 0·1 mm. (the first molecules being adsorbed at a pressure below 0·I mm. whatever the pressure value to which the final heat of sorption corresponds), thus giving rise to a somewhat high value. Again the first molecules to condense at the bottom of a narrow capillary will have a greater heat of adsorption than those in a more exposed position. Similar results have been obtained with CS<sub>2</sub> by Allmand and Lizius.<sup>7</sup>

A parallelism exists between this view of the charcoal surface and that deduced for chabasite. Partially dehydrated chabasite forms a nearly perfect molecular sieve, the porosity, therefore, corresponding to that of an ideally activated charcoal. It rapidly adsorbs the vapours of water, methyl alcohol, carbon dioxide and carbon disulphide, whereas amyl alcohol is only slightly adsorbed and vapours such as benzene, ether and carbon tetrachloride are not adsorbed at all. This indicates the effect on adsorption of the volume and length of the molecule, and hence in the present case of adsorption on charcoal one cannot compare the volume of amyl alcohol adsorbed at 0·1 mm. with the volume of carbon tetrachloride adsorbed at the same pressure.

It would appear that a probable explanation can be afforded on the grounds of this new hypothesis of the mechanism of the poisoning of a charcoal by CxOy and the subsequent drift. It will be necessary to anticipate the results in Part III. of this series in stating that drift is much more marked in under-activated charcoals, than in other cases. On the present theory the pitting in a charcoal of this type is very small (Fig. 5, II.), hence the foreign molecules which come in this area will be held by more powerful forces than if the pitting were comparatively wide. It has been suggested as a result of previous work, that the charcoal complex CXOY exists as a sponge on the surface, which is partly removed by evacuation of the charcoal and partly by flushing. The first portion comes off easily, and then its removal becomes increasingly more difficult as the amount lessens.8 Obviously the last places from which it will be removed are the active centres, and if these are situated in small depressions it will be still more difficult for the  $C_{\mathbf{X}}O_{\mathbf{Y}}$  to be removed from the points. Hence in flushing out, it will need a much higher temperature

<sup>&</sup>lt;sup>4</sup> Allmand and Burrage, Proc. Roy. Soc., 130, 610, 1931. <sup>5</sup> J. Physic. Chem., 32, 452, 1928. <sup>6</sup> Proc. Roy. Soc., 129, 235, 1930. <sup>7</sup> Ibid.,, 134, 554, 1932.

<sup>8</sup> Burrage, Trans. Far. Soc., 28, 192, 1932.

and greater pressure of the displacing vapour before these points can be freed, than if the latter were in large open cavities.

Another point which may be noted in passing is that an explanation is also afforded of the experimental fact—that the  $CO_2$  evolved is extremely small when compared with the amount of C  $Cl_4$ , for example, which is adsorbed in its place. It has been shown  $^9$  that  $CO_2$  can be adsorbed anywhere on the surface, and also that its isothermal gives rise to steps as does C  $Cl_4$ . This latter substance, however, can only be adsorbed in the region of an active point, so that when another ring of C  $Cl_4$  forms round one of these, it does so at the expense of the  $C_XO_X$ , which is freed as  $CO_2$ , the molecules of which now form a ring round the outside of the new C  $Cl_4$  ring, very few actually entering the vapour phase.

At this point it is necessary to show the relation between the degree of activation and the isothermals derived from the charcoals. In Fig. 5, five stages are shown representing diagrammatically the range from

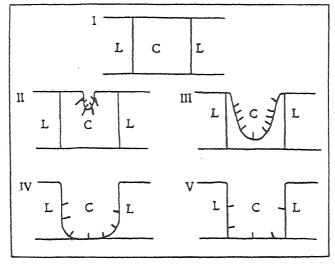


Fig. 5.

unactivation to overactivation, the squares marked L representing the charcoal derived from lignin, and that marked C—the pitted area—from cellulose.

The diagrams in Fig. 5 have the following significance:—

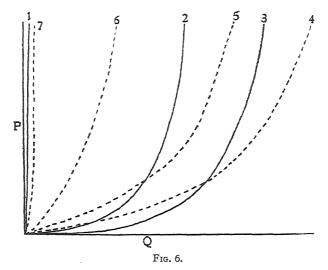
- I. Unactivated charcoal.
- II. Slightly activated.
- III. Almost the optimum activation.
- IV. Slightly overactivated.
- V. So highly overactivated as to be practically inactive.
- I. In this case there can only be adsorption if one or more of the following conditions are fulfilled:—
  - (a) In the quasi-chemical sense, if the vapour is of a suitable type, i.e., contains oxygen, nitrogen or sulphur, etc.<sup>9</sup>

<sup>9</sup> Part II. This series.

(b) If the vapour has a dipole moment sufficiently large to cause the molecules to congregate round any projection from the surface as it would in the neighbourhood of an active point. This, however, would only take place above O·I mm.

II. In this case there is a slight pitting causing an increase in the surface area and producing active points. The resultant isothermal will have a certain quantity value at low pressures and will then rise fairly sharply at almost a constant quantity value, a very small amount of substance adsorbed giving a large rise in pressure, since there are but few active points and these are in a confined space, thus allowing only a few rings of molecules to form round each point, even at high pressures, before the adjacent pools touch and so cover the surface.

III. This represents a greater surface area and therefore a greater quantity value is obtained at low pressures; at the same time there are many more active points, which will cause the quantity values in the iso-



thermal to increase rapidly at pressures corresponding to the lower

steps and then to rise vertically as in the previous case.

IV. This shows a lowering of the available surface and therefore a lowering of the quantity adsorbed at low pressures. The active points are now fewer in number and are in a larger area than in the previous case, therefore the steps will have shorter treads on the quantity axis of the isothermal, but the latter will mount steadily throughout its entire range, since many more rings can form round each active centre before the pools touch.

V. This represents the overactivated state which is almost inactive. The quantity adsorbed at low pressures will be lower still, and the isothermal will mount fairly rapidly as there are practically no active points

around which vapour molecules may congregate.

Thus with progressive activation of the charcoal, it should be possible to increase its capacity at low and high pressures, and then decrease its capacity at low, while still increasing its quantity values at high pressures Finally a stage should be reached when the capacity at high pressures.

will also decrease. This is represented diagrammatically in Fig 6, the

degree of activation being indicated by numbers.

Again from the present hypothesis it is obvious why there should be a steady decrease in the value of the apparent density with increase of activation. The view expressed above has received partial confirmation in experiments carried out on a series of charcoals which were pro-

gressively more activated. The starting product was palm nut shell and steam the activation agent. M<sub>1</sub>, M<sub>2</sub>, M<sub>3</sub> and M<sub>4</sub> have already been described.10 The apparent densities of the remaining charcoals M5 and M6 were 0.404 and 0.392 re-In Table I. are spectively. given the quantities adsorbed at 0.01 mm. and at saturation at 25° C. (115 mm.), the technique employed being that of charging and withdrawal at constant pressures.11

	inder 1.		
Charcoal.	Quantity in Mgs./Gm.		
	oʻoi mm.	115 mm.	
$egin{array}{c} \mathbf{M_1} \\ \mathbf{M_2} \\ \mathbf{M_3} \\ \mathbf{M_4} \\ \mathbf{M_5} \end{array}$	4.0 111.0 152.0 143.1 129.6	12·6 376·6 682·4 729·3 891·6	

125.0

919.5

TARIF T

If these results had been expressed as mgs./c.c. the effect would have been still more pronounced, since there is a progressive fall in the value of the apparent density with increase of activation. This series has not been carried far enough to show whether a charcoal can be so overactivated as to be practically inactive.

 $M_{c}$ 

In order to test this point a series of charcoals were made under different conditions and their capacities tested for water and carbon tetrachloride.

#### Beechwood Charcoal.

Experimental Details.—The wood chips were packed into a silica tube about 12 inches long and  $\frac{3}{4}$  inch in diameter, closed by a ground glass stopper which was fitted with a wide bore tap. This connected with a trap for the oil, evolved during charring, and two others which were surrounded with liquid air. The whole apparatus was evacuated to  $10^{-3}$  mm. by a Hyvac Oil Pump, and the wood charred at 750-800° C., the resultant charcoal being cooled in a vacuum by closing the tap on the silica container. The electric furnace was heated to the required temperature and then slid along the horizontal silica tube containing the wood chips. This unactivated charcoal will be referred to as Ex A.

A sample of this charcoal was very slightly activated by passing 0.5 per cent. oxygen in a nitrogen stream for one hour at 700°, giving rise to a dull black charcoal, Ex B, which was very dusty and friable.

A sample of the chips was immersed in a saturated solution of Phosphoric Acid for half an hour at room temperature. The solution turned a deep brown and the chips became reddish-brown. This was charred at 700° and washed with water—Ex C.

A further sample was treated with the same solution for six hours. On dilution of the liquid a white solid was precipitated showing very definitely that something had been dissolved from the wood. On analysis

J. Physic. Chem., 34, 2202, 1930.
 Burrage, Chem. News, 145, 206, 1932.

the solution was found to contain cellulose and sugar. This was charred as in the previous case—Ex. D.

Another sample of the chips was treated with HCl and ZnCl<sub>2</sub> for twenty hours at room temperature and finally for one hour at 100° C. The solution rapidly assumed a deep red colour and on dilution a large amount of flocculent reddish-brown solid was precipitated. These chips were charred in the same manner as before—Ex. E.

It was very noticeable in this case that the fibres of the wood were

TABLE II.

Charcoal.	H <sub>2</sub> O.	C Cl <sub>4</sub> .
Ex. A ,, B ,, C ,, D ,, E	56·6 mgs./gm. 78·1 ,, 67·2 ,, 55·0 ,, 44·6 ,,	6·1 mgs./gm. 11·3 ,, 15·1 ,, 14·1 ,, 12·1 ,,

tending to come apart. Microscopic examination revealed the fact that all the chemicaly activated samples were falling to pieces longitudinally with respect to the original wood. This points to the fact that the separate vessels in the original wood have become detached under the activa-

tion treatment. The resultant charcoals gave rise to granules which were fairly bright in colour, and somewhat soft and friable. These charcoals were tested with water at 12.8 mm. and C Cl<sub>4</sub> at 33 mm. at 25°.

This series shows a definite rise followed by a fall for both water and C Cl<sub>4</sub> values. According to the theory, Ex. A is unactivated, Ex. B practically the same, and Ex. C, D and E so highly overactivated as to be practically inactive. The results would appear to suggest that this is the case. A further series was carried out with ZnCl<sub>2</sub> and HCl as the activating agent and the times of activation greatly reduced, the resultant charcoal being tested with C Cl<sub>4</sub> at 33 mm. and 25° C.

TABLE III.

Charcoal,	Time of Activation.	Quantity Adsorbed.	
Ex. F	15 mins.	151·0 mgs./gm.	
,, G	30 ,,	14·1 ,,	
,, H	60 ,,	22·7 ,,	
,, I	180 ,,	14·0 ,,	

Obviously from this series to get a good charcoal the time of activation must be very short or else a much weaker solution of the activating agent must be used. It was decided to carry out a further series using charcoal made from birchwood, with the same concentration of solution as before, the times of activation being considerably lowered and the intervals being lessened between the members of the series.

## Birchwood Charcoal.

Chaney 12 considers that primary carbonisation of wood substances produces the necessary surface and capillary structure to account for all adsorption obtained in activated charcoals, at the same time certain

<sup>12</sup> Trans. Electrochem. Soc., 36, 91, 1919.

oily hydrocarbons are formed and adsorbed with great tenacity on the active carbon framework. He states further that activation is the only process by which the adsorbed hydrocarbon can be burned away without at the same time burning away the active carbon base.

The old theory, therefore, suggests that the active centres are present in an unactivated charcoal, whereas the new theory postulates that they are produced by activation. On the new theory the remnants of the cellulose after treatment with the activation agent are the potential active points. On charring, however, these will adsorb the hydrocarbons from the vapour phase, unless special precautions are taken, and thus poison themselves if the zinc chloride, for example, were not present. If this were present, it would be adsorbed by the points, which would be freed by subsequent washing.

In this series it was decided to boil the treated wood before charring to remove all the  $\mathrm{ZnCl_2}$ , to demonstrate that an active charcoal would still result. The same apparatus was used as in the previous case, the hydrocarbons in the vapour phase being very largely condensed out in the liquid air traps. It was realised that there must be a certain amount of poisoning by the hydrocarbons but this was considered to be insufficient to interfere with the general result to any marked degree. As before the resultant charcoals have been tested with C  $\mathrm{Cl_4}$  at 33 mm. and 25°.

Charcoal. Time of Activation. Quantity Adsorbed. I min. Ex. J 37.2 mgs./gm. 3 mins. 71.8 L 5 102.7 ,, 219.4  $\mathbf{M}$ 10 ,, ΙI 224.3 ,, O P Q R 258.6 12 ,, 13 251.1 ,, 14 228.2 ,, 15 157.2 ,, ,,

TABLE IV.

From Tables III. and IV. it is obvious that a charcoal can be rendered almost inactive by prolonged activation. This follows directly from the new theory of activation but cannot be accounted for by the previous one. Also it has been shown that active charcoals with varying capacities corresponding to the time of activation by the chemical agent can be prepared, although the latter was entirely removed before charring.

#### Summary.

- 1. A New Theory of Activation of charcoal has been advanced which embraces all types of activation.
- 2. The application of this theory to the mechanism of adsorption has been discussed.
- 3. A number of experiments have been carried out confirming the main outline of the new theory.

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## STUDIES ON ADSORPTION. PART II. MECHAN-ISM OF THE ADSORPTION OF VAPOURS BY UNACTIVATED CHARCOAL.

By L. J. BURRAGE.

## Received 7th December, 1932.

In some preliminary work, it was found that certain substances were readily taken up by unactivated charcoal, while others were scarcely adsorbed at all. It appeared that a detailed study of the mechanism of adsorption by unactivated charcoal would be of distinct advantage in the investigation of the mechanism of adsorption in general.

It has been deduced from an investigation into the Mechanism of

		SLE I	•		n	the Activation of Charcoal, that this process increases the surface area of the charcoal and also
	Substance.				D.	creates areas of high adsorptive
	Water .				81	potential which are capable of
	Methyl alcohol				33	inducing polarity in molecules
3. ]	Ethyl alcohol	•			26	0 i
	Acetone .	•			21.9	which are normally apolar. It
	Sulphur dioxide				16.2	was, therefore, decided to carry
	Ethyl acetate	•		٠	6.0	out a series of experiments, using
	Ethyl ether	•		•	4.0	an unactivated charcoal made
8. (	Carbon disulphi	de			2.6	
	Benzene .				2.3	from palm nut, M I,2 and deter-
io. (	Carbon tetrachle	oride			2.2	mining the sorption isothermals
						of substances whose dielectric

constants ranged from 81 to 2. The series (Table I.) was chosen.

The mechanism which governs adsorption by unactivated charcoal would appear to be that the vapour molecules may be capable of collecting round any projection or cavity on the surface, and this mechanism must, therefore, be confined to polar molecules, if the hypothesis that has been outlined is correct. This would probably mean that the  $C_XO_Y$  sponge on the surface has the power of adsorbing vapour molecules.

## Experimental.

In the case of sorption by activated charcoal vapours, such as water, are known to break up the  $C_X O_Y$  and remove it as  $CO_2$  at a slow rate, whereas others, such as  $CCl_4$  remove it fairly rapidly. Now, suppose a vapour, such as methyl alcohol, be adsorbed by unactivated charcoal, by combining with the complex (explained in detail later), and be capable of breaking up the surface  $C_X O_Y$  fairly readily, then, as a result, it will remove the agent whereby it is attached to the charcoal and the quantity of alcohol adsorbed will thereby tend to fall.

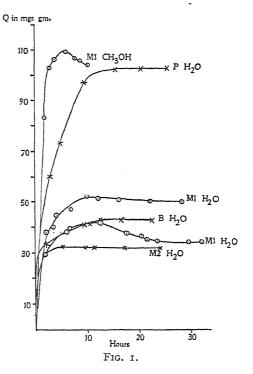
On the other hand, if all the  $C_XO_Y$  is displaced it will tend to partially activate the surface and thus cause some alcohol to be more tightly held. Thus, there will be a balance of effects in which it is considered

<sup>2</sup> J. Physic. Chem., **34,** 2202, 1930.

<sup>&</sup>lt;sup>1</sup> Part I. of this Series. Trans. Far. Soc., 29, 445, 1933.

the former will predominate at higher pressures, since some of the projections on the surface will be removed altogether, thereby causing a lessening of the total available adsorptive surface, and the activation of the charcoal surface proper will only take place when the last traces of  $C_{\mathbf{x}}O_{\mathbf{y}}$  are removed. Under these circumstances if the isothermal were to exhibit hysteresis, similarly to water, then the final reproducible curve in this case would probably lie between the original sorption and desorption curves. To substantiate this statement a short description of the probable mechanism of water hysteresis must be made, although it will only be mentioned briefly as it is treated in full in Part IV. of this series. It is considered that water forms a film over the  $C_{\mathbf{x}}O_{\mathbf{y}}$  on the surface, covering over small pores underneath. When the external

pressure of water vapour has reached a higher level, this film breaks and the pore fills with water. If the film had not been formed water would have condensed in the pore at a lower pressure, hence the sorption pressure is too high. A similar occurrence takes place on desorption when, owing to surface tension effects, the pressure over the charcoal has to be lowered considerably before the water can vaporise from the pore, hence the desorption pressure is too low. In the case of methyl alcohol this effect will probably enter to a comparatively small extent. On the other hand, during the course of the experiment more alcohol becomes quasi chemically held, which would tend to move the isothermal in the direction of a greater



quantity value for the same pressure. At the same time  $C_{\mathbf{X}}O_{\mathbf{Y}}$  is being removed and hence the quantity value of alcohol adsorbed is lowered. The probable resultant of these effects would be that the final reversible isothermal would coincide with the original sorption curve at high pressures and with the desorption curve at low pressures.

If now one takes a dry sample of unactivated palm nut charcoal and passes  $CO_2$  free air, saturated with vapour at a definite pressure, it should be possible to detect this effect. The results shown in Fig. 1 bear this out. Three experiments have been carried out with M 1 charcoal, two with water vapour and one with methyl alcohol. Three results are also added for activated charcoal and water to show the type of curve one normally obtains. (Charcoal B 3: Charcoal M 2 2: Charcoal

<sup>&</sup>lt;sup>3</sup> J. Physic. Chem., 32, 441, 1928.

P. Zinc Chloride activated peat. Apparent density = 0.329). These

experiments were carried out at 25° C.

The points do not fall exactly on the curves in Fig. I, since the sorption process has been shown (in a paper accepted by the Journal of Physical Chemistry for publication) to be discontinuous. By passing the effluent gas through baryta water, CO2 was shown to be liberated during the course of the experiment. It will be seen that all three curves for the unactivated charcoal pass through a maximum, which is in excellent agreement with the present hypothesis. It has been suggested that the fact that the quantity value passes through a maximum when charging at constant pressure may be due to breaks in the isothermal. If there are any small pores on the surface, they will be more or less filled with the CXOY sponge. This latter will adsorb water and cause condensation to take place at a lower pressure than if the pore were quite clean. When the water is adsorbed it will tend to turn off the  $C_XO_Y$  as  $CO_2$ , thereby cleaning up the pore. But it has already been stated that the water would not have condensed in the pore if it had been clean. Therefore the water which has already condensed will vaporise, thus the quantity value passes through a maximum.

It is more probable in this case that the pores are depressions in the  $C_XO_Y$  sponge, so that the water is being held by the complex. As this is turned off by the water, the pores become larger and water can no longer condense in them at this pressure. That water would appear

to be held by the CxOx is shown in Table II.

TABLE II.

		Quantity of Water at Zero Pressure.		
Method Employed.	Temperature of Evacuation.	Charcoal A.3	Charcoal C.3	
NaOH Extd. <sup>6</sup> . Static <sup>5</sup> . Static <sup>5</sup> . N <sub>2</sub> streaming <sup>4</sup> . N <sub>2</sub> streaming <sup>4</sup> . N <sub>2</sub> streaming <sup>4</sup> .	. 800° . 270° . 800° . 270° . 800°	3·15 4·28 7·67 12·6 15·4 43·5	1·58 5·74 9·92 13·7 17·5 40·0	

In all cases the isothermals were determined at 25° C.

It will be noted that the same treatment of two different charcoals causes the amounts of water held at zero pressure to fall in the same order. One cannot imagine this to be due to ash, since the amounts of the latter are dissimilar and it would thus mean that the same proportion of ash was removed in each case. It is much more reasonable to assume that the water is quasi chemically held by the partly removed  $C_XO_Y$ . It is then quite understandable why similar treatment should give rise to a similar proportion of quasi chemically held water in the case of two different charcoals. Too great a weight must not be placed on the exact amount of the figures in the nitrogen streaming experiments, as these were the result of early work. In this case zero pressure meant no change

<sup>&</sup>lt;sup>4</sup> J. Physic. Chem., **33,** 1161, 1929. 
<sup>5</sup> Ibid., 1682, 1929. 
<sup>6</sup> Ibid., 1694, 1929. 
<sup>7</sup> Part IV. of this series (unpublished work).

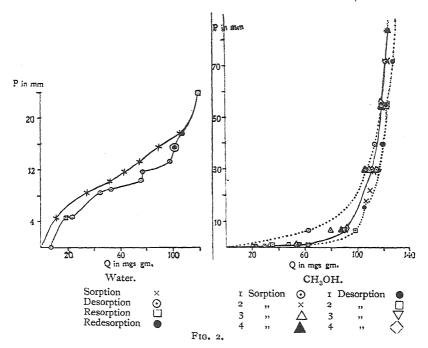
in weight after streaming at 70-80 c.c./min. for I hour, whereas in the new dynamic method zero pressure means no alteration in weight after streaming at 400 c.c./min. for 4 hours, which undoubtedly gives rise to a lower figure.

It has been shown that NaOH extraction causes the isothermals to rise almost vertically along the pressure axis. This must be due, to some extent, to a poisoning of the active centres by NaOH, but it is far more likely to be due to the removal of the  $C_{\mathbf{X}}O_{\mathbf{Y}}$  sponge to which water had been attached. This subject will be dealt with in more detail in Part IV of this series.

At this point the series of experiments to which reference has already been made at the beginning of this paper will be described. It will be necessary to give each experiment in detail and these will be dealt with under separate headings. In all cases between I and 2 gms. of charcoal were taken, and, as all weighings were carried out to 0·I mg., the results are considered to be correct to 0·I mg./gm. All isothermals have been carried out at 25° C., using Charcoal M I.

#### 1. Water.

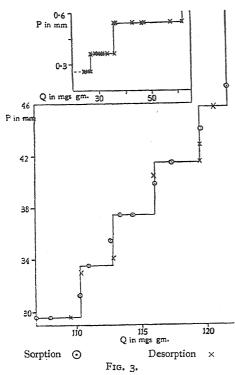
The saturating systems employed were Methods 1A and B 8 in which air was passed through a series of coils containing sulphuric acid. A complete sorption and desorption isothermal was carried out, the maxi-



mum pressure reached being 17.5 mm. This was followed by resorption to 23.76 mm. and redesorption until the previous desorption curve was reached. In order to allow equilibrium to be established as far as possible

<sup>&</sup>lt;sup>8</sup> Burrage, Chem. News, 145, 206, 1932.

the experiment was carried out over a period of three years, the charged charcoal being allowed to stand for approximately two months between each pressure reading, since isothermals with water show a marked tendency to drift.



The results are expressed in Fig. 2. The isothermal appears to be somewhat irregular, this being due to an insufficient number of points being taken to define each loop exactly. It was quite unnecessary, however, to amplify the number of points for the purposes of

## 2. Methyl Alcohol.

this experiment.

The method used for the saturation of the air stream all the following experiments was Method 2A.8 Sorption was carried out up to saturation; this was followed by desorption, then resorption and redesorption, a second and third resorption and redesorption and a final desorption of the retentivity technique. These are expressed in Figs. 2 and 3. Fig. 2 the first sorption and desorption curves have been

dotted and the final isothermal represented by continuous lines.

It will be seen that the isothermal is definitely step-like in formation. The final isothermal in Fig. 2 (continuous lines) is in between the initial

sorption and desorption is othermals. This is definitely in agreement with the general hypothesis expressed at the commencement of this paper.

The charcoal was allowed to stand for two months and then sorption and desorption points ob-

TABLE III.

Pressure in mm.	Quantity Range in mgs./gm.	Difference.
45.7	121·7 — 119·6	2·I
41.5	119·6 — 116·1	3·5
37.4	116·1 — 112·9	3·2
33.5	112·9 — 110·3	2·6
29.6	110·3 — 107·0	3·2
0·52	62·0 — 36·0	26·0
0·28	36·0 — 27·0	9·0
0·15	27·0 —	—

tained by charging and withdrawal at a constant pressure. These results are expressed in Fig. 3.

The resultant isothermal appears step-like in appearance. Its discontinuous nature cannot in any way be due to the particular method

employed, since the points were obtained by charging or withdrawal at constant pressure. The pressure at which breaks have been found to occur and the quantity increments per step have been expressed in Table III.

There is a slight tendency to conform to the water type of isothermal (unpublished work), small quantity increments per step at low pressures, then larger at intermediate pressures and finally smaller at high pressures.

## 3. Ethyl Alcohol.

A number of sorption and desorption experiments were carried out and these are expressed in Fig. 4.

Point A was obtained after standing 92 hours and showed very considerable drift, and point B after 20 hours showed slight drift, whereas point C showed no drift at all after 72 hours. Beyond point D the isothermal is reversible and has moved back towards the pressure axis. This is similar to the

experiments with CH<sub>3</sub>OH, but it is not so pronounced.

TABLE IV.

•	Pressure in mm.	Quantity in mgs./gm.
4. Acetone.	102	101.4
•	61	100.7
This was found to give reversible	13	97.9
results immediately and the figures	.5	96.7
are expressed in Table IV. It was	13	97.9
	61	100.8
noted that a fair amount of heat	IO2	101.4
was evolved during sorption.	13	97.9
- •	0.0	77.6

## 5. Sulphur Dioxide.

The charcoal was charged at 760 mm. with SO<sub>2</sub> and desorbed by the modified retentivity technique. The results shown in Fig. 4 give very definite evidence of the step-like formation of isothermals.

It is interesting to note that the lowest break is 0.06 mm., agreeing with that found for CO<sub>2</sub>. 16

#### 6. Ethyl Acetate.

A certain amount of drift was encountered, giving rise ultimately to a reversible isotherm, the figures being given in Fig. 5.

## 7. Ethyl Ether.

The charcoal was charged to saturation at 290.8 mm. and the desorption experiment carried out by the retentivity technique. The

Pressure in mm. Quantity in mgs./gm. Pressure in mm. Quantity in mgs./gm. 290.8 328.6 0.04 301.8 0.4 328.6 0.006 298.6 0.4 324.7 0.004 297.3 296.6 0.4 321.1 0.003 0.2 315.2 296.0 0.00 0.2 314.3

TABLE V.

results are shown in Table V. It was noted that a very large amount of heat was liberated during sorption.

This is very remarkable in that so large a proportion of the total quantity adsorbed at high pressures is chemically held. There is definite evidence of the step-like structure above a certain pressure and a curve below, but, owing to insufficient points the exact pressure cannot be determined. It must lie somewhere between 0.2 mm. and 0.04 mm. (In other cases investigated it was either 0.1 mm. or 0.06 mm.).

## 8. Carbon Disulphide.

Although the dielectric constant of this substance is very similar to CCl<sub>4</sub> an isotherm has been carried out for two reasons:—

(1) To assist in the investigation of the positions of charcoals under test with this vapour at low pressures compared with those obtained with CCl<sub>4</sub> at the same relative pressure, since marked anomalies have been found; 9 and

Litres.	Not retained in mgs./gm.	Litres.	Not retained in mgs./gm.
0·0	60·3	3·2	56·0
0·4	59·7	7·2	52·9
0·8	59·1	15·2	50·6
1·2	58·6	36·4	45·6

TABLE VI.

(2) To endeavour to throw more light on the statement made in a paper dealing with static measurements: 10 "These CO<sub>2</sub> pressures were far greater than those observed in other cases. Whether CS<sub>2</sub> has any particular displacing action on the surface gases is doubtful."

Some vapours turn off surface gases readily, whereas others do not. If, now,  $CS_2$  is adsorbed strongly by inactive charcoal it will probably have a large effect in turning off  $CO_2$ . On the other hand, since ac-

Litres.	Weight retained in mgs./gm.	Litres.	Weight retained in mgs./gm.
0·0 1·6 2·0 2·4 2·8 4·0	60·3 58·2 57·8 57·3 56·5 55·4	5·0 6·0 10·0 14·0 24·0	54·4 53·8 52·0 50·9 48·5

TABLE VII.

cording to its dielectric constant it should not be adsorbed, it follows that if some is adsorbed it may be because of its similarity to  $CO_2$ , thereby exerting a displacing action on the outermost molecules of the  $C_XO_Y$  complex, since the ratio of the vapour pressures is greatly in favour of the  $CS_2$ .

<sup>&</sup>lt;sup>9</sup> Burrage (unpublished work).

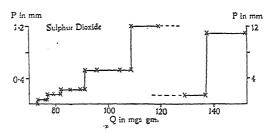
<sup>10</sup> Allmand and Burrage, Proc. Roy. Soc., 130A, 610, 1931.

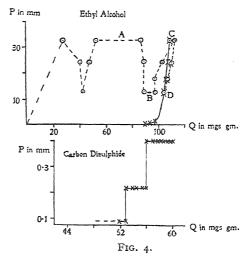
The charcoal was saturated with vapour at 127.9 mm. pressure and the desorption carried out by the modified retentivity technique, the figures for which are given in Table VI.

A resorption experiment was carried out at the original charging pressure and the initial quantity of 60·3 mgs./gm. was again obtained. A second desorption experiment was carried out, the results being given in Table VII.

The resultant isothermal from the two sets of figures is given in Table VIII. and Fig. 4.

If CS<sub>2</sub> is a much better agent than CCl4 for removing  $C_XO_Y$ , as has been suggested in a previous publication,11 it will probably remove the complex almost completely. Hence the surface will be partially activated in the process. To test this, at the close of the experiment dry air was passed through the container at 150° for 1½ hours, less than 0.5 mgs./gm. CS<sub>2</sub> being retained. It was tested





with CCl<sub>4</sub> at 33 mm., 4·3 mgs./gm. being adsorbed as compared with 12·4 mgs./gm. on a fresh sample. There is thus a definite poisoning effect and certainly no activation of the charcoal surface. Any activa-

TABLE VIII.

Pressure in mm.	Quantity Range in mgs./gm.	Difference.
0·4	60·3 — 56·0	4·3
0·22	56·0 — 52·9	3·1
0·09	52·9 — 50·6	2·3

tion which may have taken place cannot be masked by oxygen going back on the charcoal to form the CxOx, for CCl<sub>4</sub> would remove this in the same way as it removes the com-

plex from the active centres in the case of activated charcoals. Hence the minute amount of  $\mathrm{CS}_2$  which is left on the charcoal has not been turned off by the large  $\mathrm{CCl}_4$  pressure but poisons the surface in a similar fashion to  $\mathrm{C}_X\mathrm{O}_X$ . This would tend to show that  $\mathrm{CS}_2$  is being adsorbed in the same manner as  $\mathrm{CO}_2$ .

<sup>11</sup> Allmand and Lizius, Proc. Roy. Soc., 134A, 555, 1932.

#### o. Benzene.

The experiment consisted of a desorption followed by a sorption isothermal, the results being given in Table IX.

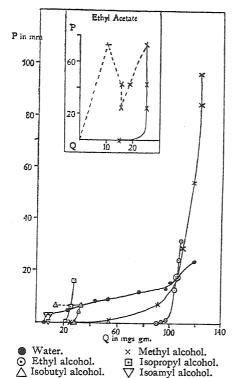


FIG. 5.

Т	`A	B	LE	T	X

Pressure in mm.	Quantity in mgs./gm.
75.9	11.6
45.7	11.7
23.9	10.4
45.7	11.5
75.9	11.6

#### 10. Carbon Tetrachloride.

A desorption, sorption and second desorption series were carried out, the results being expressed in Table X.

TABLE X.

Pressure in mm.	Quantity in mgs./gm
91	9.5
57	7.1
33	7·1
57	11.2
91	12.4
57	12.4
33	12.4
0	4.0

Experiments have also been carried out with isopropyl, isobutyl and isoamyl alcohols

and these have been expressed in Fig. 5 together with the final isothermals of water, methyl and ethyl alcohols.

## Discussion.

In the original hypothesis it was suggested that the mechanism of adsorption by unactivated charcoal was that polar molecules would congregate round any projection from the surface in a similar manner to round the active points in an activated charcoal, whereas apolar molecules would scarcely be adsorbed. This was not found to be correct in every case, however, as ethyl acetate (D=6) was only very slightly adsorbed, whereas ethyl ether (D=4) was very strongly adsorbed.

It was noted for some substances that the isothermals remained at a practically constant quantity, whatever the pressure, whereas others showed the normal type of isothermal curve. The amounts of substance retained at zero pressure, which can be considered as practically chemically held, however, varied enormously. If this amount be subtracted from all the maximum saturation values, expressed as the fraction of a mol. adsorbed per gm. of charcoal, the order is practically

that of the Dielectric Constants shown in Table XI, but does not fall in the same order as the natural dipole moments.

TABLE XI.

Substance.	Dielectric Constant.	μ.	mol./gm.
Water Methyl alcohol Ethyl alcohol Acetone Sulphur dioxide Ethyl acetate Ethyl ether Carbon disulphide Benzene Carbon tetrachloride	81 (18°) 33 (18°) 26 (18°) 21·9 (15°) 16·5 (18°) 6·0 4·0 (18°) 2·6 (18°) 2·3 (18°) 2·2 (18°)	1.85 × 10 <sup>-18</sup> 1.68 ,, 1.72 ,, 2.84 ,, 1.76 ,,	0.006 0.004 0.0005 0.0004 0.003 0.0001 0.0003 0.0002 0.0001 0.00005

In view of the enormous difference existing in the amounts of these substances which were quasi-chemically held, a further investigation was carried out, some thirty different substances being examined. The procedure adopted was to charge the charcoal M I at approximately two-thirds the saturation pressure at 25° and desorb to constant weight. (In practice till no change in weight could be observed in half-an-hour when passing the air stream at 400 c.c./min.)

The complete results are expressed in Table XII.

TABLE XII.

Substance.		Pressure.	Quantity Adsorbed.	Mol./gm. at Zero Pressure.	
Ether		290·8 mm.	328·6 mgs./gm. 296·0 ,,	0.004	
Ethyl alcohol .	•	32.6 ,, 0.0 ,,	112·5 ,, 90·1 ,,	0.002	
Acetone	•	102·0 ,, 0·0 ,,	101·4 ,, 77·6 ,,	0.001	
Methyl alcohol .	•	122·2 ,, 0·0 ,,	145.0 ,,	0.0008	
Isopropyl alcohol	٠	16·1 ,, 17·9 ,, 6·0 ,, 16·1 ,, 17·9 ,,	27.4 ,, 27.4 ,, 24.5 ,, 27.4 ,, 27.4 ,, 21.0 ,,	0.0004	
Isobutyl alcohol	•	6·5 ,, 4·I ,, 6·5 ,, 4·I ,, 6·5 ,, 0·0 ,,	14·3 ", 14·3 ", (Stood 24 hrs.) 33·1 mgs./gm. 31·3 ", 33·1 ", 27·7 ",	0.0094	

TABLE XII. (Cont.).

Substance.		Pressure.	Quantity Adsorbed.	Mol./gm. at Zero Pressure.
Water	•	17.5 ,,	105.6 ,,	0.0003
Acetic acid .	•	0·0 ,,	19.9 ,,	0.0003
Ethyl acetate .	•	72·8 ,, 0·0 ,,	25·1 ,, 15·1 ,,	0.0002
Isoamyl alcohol	•	3.0 ,, 3.0 ,, 3.5 ,,	6·2 ,, (Stood 24 hrs.) 9·7 mgs./gm. 9·7 ,,	
Carbon dioxide .		0.0 ,,	8.3 ,,	0.00009
Benzaldehyde .		0.0 ,,	2.9 ,,	0.00007
·	•	0.01 "	2.0 ,,	0.00002
Hydrogen sulphide	٠	760·0 ,, 0·0 ,,	94·I ,, 45·9 ,,	0.001
Sulphur dioxide .	•	760·0 ,, 0·0 ,,	249·2 ,, 73·0 ,,	0.001
Carbon disulphide	•	127·9 ,, 0·0 ,,	60·3 ,, 45·6 ,,	0.0006
Ethyl sulphide .	•	32·0 ,, 0·0 ,,	25.5 ,,	0.0002
Thiophene		31.1 ,,	23.2 ,,	0.0001
Mono nitro methane		18.0 ,,	125.5 ,,	0.001
Ammonia		100.0 ,,	48.5 ,,	
N. propylamine .		9.0 ,,	19·6 ,, 59·4 ,,	0.001
Piperidine	-	0·0 ,, II·2 ,,	34.9 ",	0.0006
Aniline		0·01 ,,	18.5 ,,	0.0002
Pyridine		0.0 ,,	7.0 ,,	0.00009
	-	4·2 ,, 0·0 ,,	4.6 ,, 4.6 ,,	0.00000
Chloroform .	-	100.0 ,,	22.8 ,,	0.00006
Ethyl iodide .		70.0 ,,	7·3 ,, 28·6 ,,	
Carbon tetrachloride		o·o ,,	8.5 ,,	0.00005
Benzene		o·o ,, 75·9 ,,	4.0 ,, 11.6	0.00003
Monochlorbenzene		0-0 ,,	2.0 ,,	0.00003
Zamor deliseite		4.9 ,, 0.0 ,,	8.6 ,,	0.00001

In Table XIII the amounts held at zero pressure are expressed in fractions of a mol/gm. charcoal and the substances placed in their order of merit, being grouped in four sections, (I) those containing oxygen, (2) those with sulphur, (3) those with nitrogen, and (4) the substances which do not contain any of the above elements.

From the previous table it will be seen that only substances containing oxygen, sulphur or nitrogen have any appreciable amounts tightly held, therefore it would appear that the molecules are held to the charcoal surface, or the partly removed  $C_{\mathbf{X}}O_{\mathbf{Y}}$  sponge, as oxonium, sulphonium or ammonium compounds. It would appear to be probable that arsenic and phosphorus would act in a similar fashion, but these cases were not investigated. The nature of the linkage of the above atoms has a large effect on the amounts of substance quasi-chemically held, the simpler being the substance the greater the amount. There are one or two exceptions to this, e.g., water and to a lesser extent methyl alcohol. One would expect a fair amount of these latter substances to be adsorbed at higher pressures, since they have high dielectric constants. This

#### TABLE XIII.

(:	τ)		(3)		
Ether .		0.004	Mono nitromethane		. 0.001
Ethyl alcohol .		0.002	Ammonia		. 0.001
Acetone .		0.007	N. propylamine.	•	. 0.0006
		0.0008		•	
Methyl alcohol			Piperidine .	•	. 0.0002
Isopropyl alcohol		0.0004	Aniline		. 0.00000
Isobutyl alcohol		0.0004	Pyridine		. 0.00006
Water		0.0003			
Acetic acid .		0.0003	(4)		
Ethyl acetate .		0.0002	Chloroform .	_	. 0.00006
Isoamyl alcohol		0.00009	Ethyl iodide .	•	. 0.00002
Carbon dioxide		0.00007	Carbon tetrachloride	•	
Benzaldehyde .		0.0000		•	. 0.00003
Denzardenyde .	•	0 00002	Benzene	•	. 0.00003
10	2)		Monochlorbenzene	•	. 0.00001
•	-)				
Hydrogen sulphide		0.001			
Sulphur dioxide		0.001			
Carbon disulphide		0.0006			
Ethyl sulphide					
Thiophene .	•	0.0001			•
imophene .		0.0001			

is quite definitely what is found in practice, as is shown by Fig. 5. For the sake of comparison it would have been preferable to plot relative vapour pressures, but since the higher the pressure of vapour employed, the greater is the cleaning-up effect, it was decided to plot actual pressures and so bring out this point. At low pressures the quantity value of the water isothermal is least, then methyl alcohol and finally ethyl alcohol. At high pressures exactly the reverse is the case.

The isoalcohols are somewhat doubtful as to their exact position owing to drift effects. They tend to clean up the surface of the charcoal, but do so slowly, as the saturation vapour pressure is so small. Under the circumstances one would expect a slight increase of vapour pressure to give rise to a large cleaning up effect. This is shown in a remarkable fashion in an isothermal of amyl alcohol. Another exception is  $CO_2$ , but this is not surprising since the surface is more or less covered with a spongy mass of  $C_XO_Y$  at the start, hence one only measures the increase of  $CO_2$  which has been added to the complex in the course of the experiment and not the total combined oxygen on the surface.

Two factors governing the adsorption of substances by unactivated charcoal have already been mentioned, but it is necessary to examine the nature of the chemically combined substances more closely. The charcoal surface is always covered with a carbon complex which would appear to be a large spongy mass on the surface, with the lowest molecules chemically held and the outermost molecules practically unattached giving rise at ordinary temperatures to a definite vapour pressure of  $\mathrm{CO}_2$ . Substances like water and methyl alcohol would appear to remove these outer molecules and then attach themselves to the  $\mathrm{C}_{\mathrm{X}}\mathrm{O}_{\mathrm{Y}}$ . They would undoubtedly appear to have a very slow effect on the removal of the main portion of the complex. It has been found that substances with high vapour pressures are most effective in removing the complex, as one would have anticipated. This may be a possible reason why so little benzaldehyde and aniline should be adsorbed, although containing oxygen and nitrogen respectively, for their vapour pressures are so low.

TABLE XIV.

Supstance.			Pressure in mm.	Quantity in mgs./gm. at 25°.	Fraction Mol./gm. at Zero Pressure.
Carbon disulphide .		•	128 0.0	106·4 74·3	0.001
Sulphur dioxide .			760 0.0	225·I 45·6	0.0006
Ether	. ,		291 0·0	46·9 38·1	0.0005
Water	, ,		0.0 11.0	54·5 9·7	0.0005
Monochlorbenzene .	. ,		4·9 o·o	14·9 6·1	0.00005
Carbon tetrachloride		•	33·0 0·0	16·6 4·0	0.00003

On the other hand, ether with a very high vapour pressure is strongly adsorbed, a large amount of heat being evolved in the process. From this it would appear that substances which cause a thorough cleaning up of the surface, combine with the exposed atoms of the charcoal surface proper, whereas other substances combine with the partly removed  $C_XO_X$ . In view of the results which have been obtained it was decided to carry out a series of experiments, using an unactivated birchwood charcoal Ex. A. (Full details of its preparation have been given in Part I of this series.) These results are given in Table XIV.

It will be of interest to compare this series with the corresponding series using M I—Table XV—the quantities being expressed as mols/gm.

The charcoal M I was used after being stored in a moist condition for several years, whereas charcoal Ex. A. was used immediately it had been made. Each charcoal was dried in an air stream at 150° before use. In the case of Ex. A this would cause no change, as the charcoal

had never come into contact with water vapour, but in the case of M I all the water except a very slight amount would be removed. This very small amount, however, will most probably play an important part. It has been stated the water turns off  $C_{\mathbf{X}}O_{\mathbf{Y}}$  slowly from the charcoal surface, so that water vapour in the course of standing in contact with the charcoal over a period of years may be assumed to have exerted a fairly thorough cleaning effect. It has been shown that the more complete is the cleaning up, the more water is held at zero pressure. Hence the presence of these very small amounts of water vapour adsorbed

TABLE XV.

Substance.		Ex. A.	Ex. E.	M I.
Carbon disulphide Sulphur dioxide Ether Water Monochlorbenzene Carbon tetrachlorid	e	0.001 0.0006 0.0005 0.0005 0.00005 0.00003	0.002 \$0.0008* \$0.002* 0.0008 0.0002 0.0003 0.00006	0.0006 0.001 0.004 0.0003 0.00001 0.00003

\* After recharging. (For column Ex. E see Table XVII, page 472).

by the active centres exerts a protecting effect and prevents oxygen going back on to the active centres, and since other vapours turn off this water more readily than they remove  $C_XO_X$ , it follows that the surface of charcoal M I may be considered to be much cleaner than that of Ex. A.

Since M I is a much denser charcoal than Ex. A, one would expect the surface to be greater in the former case, hence the amounts of vapour adsorbed by M I should be greater than by Ex. A. However, this was not found to be so in every case. It is preferable not to take carbon tetrachloride and monochlorbenzene into account, as the amounts adsorbed are so very small.

TABLE XVI.

Substance.		Ex. A.	М т.
Carbon disulphide	: :	106·4 mgs./gm.	60·3 mgs./gm.
Sulphur dioxide		225·1 ,,	249·2 ,,
Ether		46·9 ,,	328·6 ,,

Water is known to be adsorbed to a greater extent by nut than by birchwood charcoal at intermediate pressures, since the morphological structure exerts considerable influence on the tendency for condensation to occur (cf. Part IV of this series). The amounts adsorbed at high pressures for the remaining three substances are given in Table XVI.

This is an interesting series, for when a comparison is made between the quantities of vapour adsorbed by Ex. A and M I, the former has the larger value for carbon disulphide, the latter for ether, and they are both practically the same for sulphur dioxide. It is known that soft wood charcoals have a greater amount of tenaciously held complex than nut charcoals, as is instanced by the effect of 800° evacuation on a carbon tetrachloride isothermal. The quality value on the isothermal of the nut charcoal has increased to the extent of a few per cents., whereas that for the soft wood has increased almost 100 per cent. It has already been stated that since M I has sorbed water from the atmosphere it will be cleaned up to a considerable extent and will thus have still less complex on the surface than Ex. A.

From this it would appear that the ether isothermal is poisoned by a very thick layer of the complex, *i.e.*, under the conditions of the experiment the ether is unable to clean up the surface, and combine with the atoms of the carbon surface proper, or else that the available charcoal surface is, in this case, extremely small when compared with that of

Substance.		Pressure in mm.	Quantity in mgs./gm.	Mol./gm. at Zero Pressure.
Carbon disulphide		127.9	211.7	
•		0.0	135.0	0.005
Sulphur dioxide .		780·0	285.8	
1		0.0	54.2	0.0008
		780∙0	315.7	
		0.0	119.6	0.002
Ether		313.5	127.8	
		0.0	61.9	0.0008
Monochlorbenzene		4.9	42.7	
		0.0	38.4	0.0003
Water		12.8	44.6	
		0.0	4.1	0.0002
Carbon tetrachloride		33.0	12.1	
		0.0	9.0	0.00000

TABLE XVII.

M r. It seems reasonable to suppose that the carbon disulphide can combine with the partly removed complex. Hence the more complex present, the greater will be the amount of carbon disulphide adsorbed. This would satisfactorily account for so large an amount of carbon disulphide adsorbed. Sulphur dioxide will function in a somewhat similar manner to carbon disulphide, but one would not expect the the ratio of the amount adsorbed by the two charcoals to be the same, since the  $\text{CS}_2$  must be anchored through its sulphur atoms, but the  $\text{SO}_2$  may be anchored by any of its constituent atoms, to the partly removed  $\text{C}_X\text{O}_Y$ , in which Rhead and Wheeler assume several carbon molecules to hold one oxygen molecule.

In the course of another series of experiments a charcoal was so overactivated (Part I of this series) as to become practically inactive as regards the adsorption of a non-polar substance such as CCl<sub>4</sub>. A

Allmand and Chaplin, Proc. Roy. Soc., 129A, 235, 1930.
 Allmand and Puttick, Proc. Roy. Soc., 130A, 197, 1930.

series of experiments has been carried out on this charcoal Ex. E, so that a direct comparison might be made with Ex. A. The complete results are expressed in Table XVII, and a comparison of the amounts. which are tightly held, made with other data in Table XV.

At high pressures, sulphur dioxide, carbon disulphide and ether are all exerting a large cleaning-up effect as well as functioning in the previous manner. This is shown by the drift in the sulphur dioxide isothermal on recharging. This, however, was not found to be the case with the other substances under similar conditions. Carbon disulphide, sulphur dioxide, ether and monochlorbenzene show substantial increases in the quantities adsorbed at high pressures, when compared with charcoal Ex. A, while water is distinctly less. The latter result was to be expected since so much complex has been removed, to which the water had been previously attached. This will be dealt with more fully in Part IV. Reference to Table XIV shows that the amounts which are tightly held are in every case greater than in the unactivated charcoal, except for water, the reasons for this having been given previously. Quite apart from the tendency to clean up the charcoal, the available surface area for such substances as CS<sub>2</sub>, SO<sub>2</sub>, etc., has been greatly increased during the overactivation process.

It would seem that this investigation tends to shed a certain amount of light on the swelling of charcoals. Rakovsky 14 makes this statement: "The fact is that water only in an old charcoal which has been stored under ordinary conditions for not less than a year behaves independently of the charcoal. In freshly obtained charcoal, or in that which has in any way been influenced by external factors, water changes its qualities during the storing of the charcoal in the course of the first year." From this it would appear that it takes a year for the adsorbed water to turn off the  $C_XO_Y$  to which it is attached and thus clean up the surface.

Although the work was carried out so long ago it would appear that a possible explanation may be afforded on the basis of the present theory. Wallace 15 stated that, "a ton of new and dry charcoal fills a space of about 48-50 cu. ft., while a ton of old charcoal will occupy no more than 40 cu. ft. As there is little change in the absolute specific gravity of the charcoal, the change in the apparent density must be due to decrease in the pore space." In a previous publication 16 it has been suggested that the CxOy exists on the charcoal surface as a spongy mass, which has been built up by combination with oxygen. The first molecules to be adsorbed are practically chemically held by this spongy material. This will undoubtedly give rise to an increase in the apparent size of the charcoal as the vapour molecules are adsorbed in the sponge. It is suggested that it is the expansion of the spongy  $C_XO_Y$  on the surface and not that of the charcoal proper which gives rise to the observed expansion effects. Water, however, gradually removes this complex; as this sponge of  $C_XO_Y$  is removed as  $CO_2$ , so the charcoal volume will shrink, giving rise to a much tighter packing. The absolute specific gravity of the charcoal would not be perceptibly changed under these conditions. In the light of the present work this appears to be a much more reasonable suggestion than a decrease of pore space.

J. Russ. Phys. Chem. Soc., 49, 371, 1917.
 Chem. News, 17, 249, 1868.
 Burrage, J. Physic. Chem., 36, 2272, 1932.

Again, Wallace states that new charcoal will hold 80-100 per cent. water, while old charcoal will hold only 30-45 per cent. This carbon complex will more or less fill the micropores of the charcoal, hence when adsorption takes place water will condense in those pores at a lower pressure than if the pore were quite clean. Thus as the water removes the  $C_XO_X$ , the quantity of water adsorbed at that pressure will fall. (Additional evidence for this will be advanced in Part IV of this series.) This is in addition to the water which is adsorbed directly by the  $C_XO_X$ , which, of course, will become less also as the  $C_XO_X$  decreases. This phenomenon would again appear to be capable of explanation by the present hypothesis.

The work of Bangham and Fakhoury <sup>17</sup> on the swelling of charcoals would appear to be connected with this. It is interesting to note that the four substances used originally (H<sub>2</sub>O, CO<sub>2</sub>, NH<sub>3</sub> and SO<sub>2</sub>) all contain either oxygen, nitrogen or sulphur in a simple molecule which has been shown to be capable of being adsorbed by the partly removed carbon complex. Again they note that, using pyridine, a small amount gives a large and immediate expansion, which, on standing, decreases. The rate of drift is accelerated by heating, after which treatment there is a much smaller tendency to drift. This points strongly to a removal of the more loosely attached portions of the complex, but a large proportion would still be undisplaced and, in fact, could only be removed by repeated flushing with the vapour concerned.

They found that benzene behaved similarly under certain conditions. The fact that benzene was adsorbed, whereas in the present work it was not, showed that the charcoal had probably been very slightly activated during the evacuation treatment, as it must be if the  $C_XO_Y$  were completely removed. In the present work the conditions are more satisfactory in that there has been no evacuation to aid the removal of surface complex, so that whatever  $C_XO_Y$  has been removed from the surface of the charcoal proper is a result of the cleaning-up powers of the vapour concerned. In this manner one is able to gauge the relative powers of

different vapours for this purpose. In a recent publication by the same authors, 18 there are a number of statements which may well be examined on the basis of the present hypothesis. It was stated that "Measurements of the expansion produced on immersing, in different liquids, pieces of the charcoal which had been variously treated brought to light the important fact that vacuum heating above a certain temperature brings about a considerable reduction in the effect." This follows directly from the present hypothesis which suggests that the expansion takes place in the  $C_XO_Y$  sponge which covers the surface. This is partially removed by evacuation, the higher the temperature the greater the amount removed, hence one would expect a lessening of the expansion effect after this treatment. They state that uncontrolled variations, amounting sometimes to as much as 30 per cent. of the expansion value for a given value of the quantity adsorbed, occurred between one experiment and another. This obviously follows from the present work, for the expansion depends directly on the amount of  $C_XO_Y$  present and it is not possible to control this factor. Another important point they notice is that only a very small amount of non-condensible gas was disengaged from the charcoal by the benzene in the course of each experiment. Their freezing agent was

evidently solid  $CO_2$  moistened with some organic liquid, and  $CO_2$  will have an appreciable vapour pressure at this temperature. As the charcoal was originally evacuated at 560° C., the majority of the  $C_XO_Y$  comes off as  $CO_2$  at room temperature, hence the disturbing element which should have been detected during the course of the experiment was  $CO_2$ .

An experiment was tried to see the effect of an oxygen-covered surface. This gave rise to an expansion which fell after prolonged evacuation. Benzene was sorbed on this surface and the result left no doubt that oxygen increased the expansion for a given quantity of benzene. The rate of adsorption was also much reduced. By repeated charging the charcoal with benzene and vacuum heating it, this oxygen effect was gradually removed. All these results follow directly from the present hypothesis. By sorbing oxygen on the surface the maximum amount of C<sub>v</sub>O<sub>v</sub> is built up, which gives rise to an expansion. On evacuation part of this is pumped away and the effect lessens. When benzene is adsorbed, however, there would be far more C<sub>X</sub>O<sub>Y</sub> on the surface than in a charcoal evacuated under normal conditions and hence the resultant expansion effect should be greater in the former case. By the repeated charging of the charcoal and vacuum heating, it would be flushed out in a manner which has been suggested by the author, 19 thus providing a cleaning-up effect, the  $C_XO_Y$  being removed and the expansion due to oxygen, therefore, disappearing. During this process CO<sub>2</sub> will be evolved, which has been shown by the author to give rise to slow equilibrium.<sup>20</sup> In some experiments carried out at 0° C., the fact that the values of molecular expansion on admitting the vapour were far higher than those at room temperature, suggests that there is less tendency for a vapour to clean up the surface as the temperature is lowered, a fact which had been previously noted by the author.

Five adsorption experiments with water were carried out from  $-30^{\circ}$  to 100° C.; in the latter experiment, however, there was no expansion, although some 7 mgs./gm. water were adsorbed. It would appear from this that the  $C_{\rm X}O_{\rm Y}$  has been removed as completely as possible at this temperature, which, being the highest, should give rise to the maximum cleaning-up effect.

In conclusion, the mechanism of adsorption by unactivated charcoal would appear to be very complex and can be classed under a number of headings:—

- I. At high pressures adsorption takes place according to the magnitude of the dielectric constant.
- 2. The higher the vapour pressure of the substance concerned the more effective will be the removal of the surface complex which may either increase or decrease the amount adsorbed.
- 3. Certain definite amounts of adsorbed vapour are quasi-chemically held, the amount being dependent on certain atoms and their position in the molecule.
- 4. Some substances can combine with the complex itself and only remove the  $C_XO_Y$  very slowly.

<sup>&</sup>lt;sup>19</sup> Trans. Far. Soc., 28, 192, 1932.

<sup>&</sup>lt;sup>20</sup> Accepted by J. Physic. Chem. for publication.

## Summary.

An investigation has been carried out on the mechanism of the sorption of vapours by unactivated charcoals.

Some ten isothermals have been determined at 25° C. for substances

whose dielectric constants ranged from 81 to 82.

An examination has been made of the various amounts of substances which are quasi-chemically held and their dependence on the nature of the particular compounds concerned.

An hypothesis has been advanced to cover this field of adsorption, and

the swelling of charcoals examined from this viewpoint.

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#### SURFACE TENSION MEASUREMENTS NON-AQUEOUS COLLOIDAL SOLUTIONS.

By E. W. J. MARDLES.

Received 24th November, 1932.

Although gelatin, night blue dye, potassium oleate, etc., lower the surface tension of water to a marked extent, even when present in very small amounts, this characteristic behaviour of surface tension depression is not always observed when the colloidal substances are dispersed in organic liquids. Usually, if the liquid has a low surface tension such as is the case with ethyl ether or acetone, the organosol has a surface tension either slightly greater or the same as the pure dispersing liquid. Thus, the additions of mastic resin, chlorophyll, copper oleate, or dragon's blood resin to ethyl ether raised the surface tension slightly, whilst potassium oleate, tannic acid, shellac, night blue dye and other colloidal substances were found to raise the surface tension of ethyl alcohol by a small amount. Similarly, cellulose nitrate and several of the above substances named increased the surface tension of ether-alcohol mixtures.1

It has been assumed that the dyes, soaps, resins and other high molecular weight substances form organosols because many of these substances partake of the character of colloids with regard to viscosity behaviour,

gelation, swelling, etc.

Although, as W. Ostwald has shown from dialysis experiments in 97 per cent. alcohol,2 many of the solutions are at least partly molecularly dispersed especially at high dilution, yet with higher concentration the individuals unite to coarser aggregates. Ostwald has classified many of these substances as "poly-dispersed" that is, they contain both molecular aggregates and coarser aggregates, presumably in a definite equilibrium ratio.

In addition to this molecular complexity, it is well known that the naturally occurring resins, celluloses, etc., are heterogeneous, and can be separated into fractions of different viscosity, etc.

Mardles, J.C.S., 127, 2940, 1925.
 Ostwald, "The Physics and Chemistry of Colloids," Faraday Society: General Discussion, 1920. Appendix to vol. 16.

Some dialysis experiments were carried out using cellulose acetate thimbles, prepared by swilling out a test tube with a 5 per cent. cellulose acetate solution and allowing the tube to drain and the remaining film to dry slowly. Dialysis occurred with the resins in benzene solution.

Freundlich and Neumann <sup>3</sup> reported that the dyes, night-blue, crystal violet, etc., lowered the surface tension of water but raised that of alcohol, whilst similarly Bircumshaw <sup>4</sup> found that potassium oleate began to lose its action in depressing surface tension when alcohol was added to the hydrosol; the authors attributed this behaviour to a fundamental change from the colloidal to the crystalloidal state, and although this conclusion might be applicable to some dyes or potassium oleate it does not appear possible for the high molecular weight and typically colloidal substance gelatin to assume crystalloidal characteristics in an organic liquid such as a mixture of acetic acid and phenol even though it does raise the surface tension. When ethyl alcohol, acetic acid, pyridine or acetone were added to hydrosols of gelatin the depression in surface tension of the sol below that of the dispersing liquid disappeared until eventually the colloid raised the surface tension.<sup>5</sup>

A study has been made of the change of surface tension with composition of binary mixtures of solvents containing colloidal substances; in those cases when the colloid depresses the surface tension of water and raises that of the organic liquid there is a particular mixture of solvents which is unaffected by the colloid with regard to surface tension change. The position of this "neutral point" cannot be calculated from the surface tension values of the sols in the pure liquids; similarly, in some instances where the surface tension of both solvents is either raised or lowered the effect varies considerably with the composition. Thus, with cellulose acetate in a mixture of aniline and o-chlor phenol the surface tension-composition curve shows a minimum with the mixture of lowest solvent power whilst in a mixture of cyclo-hexanone and benzyl alcohol the surface tension of the optimum solvent mixture is lowered less by the cellulose acetate than that of any other mixture.6 These results correlating surface tension of the sols with the degree of dispersion undoubtedly indicate that with an approach to a true solution with its high degree of dispersion there is a loss in power of depressing the surface tension of the dispersing medium.

Although the solubility of gelatin (determined directly and indirectly from gelation data and rigidity of the gels) is apparently not altered appreciably, or is in many cases slightly diminished by the additions of small amounts of acetone, alcohol, etc., to its hydrosols, yet there is no surface tension depression. It is thus necessary in dealing with the surface tension behaviour to consider the relative specific characters of the dispersing medium and colloid as well as any transition from the colloidal to the crystalloidal state. Again, cellulose esters lower the surface tension of some organic liquids, e.g., aniline, amyl acetate, benzyl alcohol, etc., whilst they raise that of acetone, acetic acid, etc. A similar behaviour is found with other colloidal substances, e.g., resins, tannic acid or dyes.

It is apparent that these differences cannot be explained by differences in the degree of dispersion.

<sup>&</sup>lt;sup>3</sup> Freundlich and Neumann, Z. Chem. Ind. Koll., 3, 80, 1908.

<sup>&</sup>lt;sup>4</sup> Bircumshaw, J.C.S., 123, 91,1923. <sup>5</sup> Mardles, Biochem. J., 18, 215, 1924. <sup>6</sup> Ibid., J.C.S., 125, 2244, 1924. <sup>7</sup> Ibid., Koll. Z., 57, 183, 1931.

In dealing with crystalline substances or mixtures of liquids, it is common experience that only with liquids of high surface tension, such as water for example, can a strong lowering effect take place, whilst in the case of liquids of low surface tension such as ether, substances usually behave as "surface inactive," only a slight rise of surface tension being observed with increase in concentration of the solute. There appears to be no reason why colloids should differ greatly in this respect from crystalloids; the raising of the surface tension of alcohol by potassium oleate or by dyes so conforms with the general behaviour.

The following experimental work of surface tension measurements was carried out by means of the drop-weight method, Harkins and Brown, and by the maximum bubble pressure method, Sugden. The drop method was specially suitable for the more viscous sols whilst the bubble pressure method was found to be very convenient in determining the temperature coefficient of the surface tension of the sols. Several measurements were made by bubbling dry hydrogen through the sols in order to note if any differences from the results obtained with air could be detected. The differences were found to be very small and apparently were of the same order of size as that of the experimental error; the experimental results given in the following tables were obtained by bubbling air through the sols or allowing the drops to form in an atmosphere of air containing the vapour of the dispersion medium.

The surface tension values obtained by the two methods used were found to be closely similar; thus, cellulose acetate by the drop weight method lowered the surface tension of benzyl alcohol, at 22° C., concentration 2 grs./100 c.c., by 3.0 per cent. and 2.9 per cent. by the maximum bubble pressure method.

With acetone, cellulose acetate of concentration 5 grs./IOO c.c. raised the surface tension from 23 to 24.45 dynes/cm. as determined by the bubble pressure method, and from 23 to 24.3 by the drop weight method.

Surface Tension and Concentration.—When the colloidal substance was found to raise the surface tension of a liquid, usually the effect when small amounts were added, was approximately proportional to the amount dispersed,

$$\Delta = (\sigma_s - \sigma_m)/\sigma_m,$$

where  $\sigma_s$  is the surface tension of the sol and  $\sigma_m$  that of the dispersion medium, or  $\Delta=MC$  where M is a constant and C the concentration of colloid, a finding which is similar to that from general experience with most crystalline substances which raise the surface tension of a liquid. In the case of tannic acid in ethyl alcohol the increase in surface tension was approximately 0.07 dyne/cm. per gram addition to 100 c.c., and with acetone-washed shellac in ethyl alcohol determined with concentrations up to 50 grams/100 c.c., the surface tension raising effect was approximately 0.06 dynes/cm. per gram addition to 100 c.c. With colophony in acetone at 20° the effect was equivalent to 0.05 dynes/cm. per gram addition to 100 c.c. Further results are shown in Fig. I. It will be noticed that with cellulose nitrate in some ether-alcohol mixtures, and with potassium soaps in alcohol, the increase in surface tension apparently becomes smaller with increasing concentration of

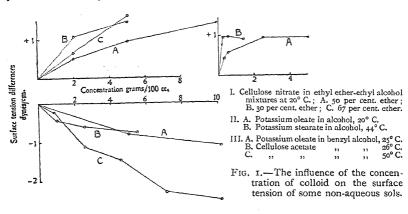
<sup>8</sup> Harkins and Brown, J. Am. C. S., 41, 499, 1919.
9 Sugden, J.C.S., 125, 27, 1924.

the colloid. This might be ascribed to a fall in the degree of dispersion with rise of concentration. In the case of potassium stearate in alcohol at 44° C. the limit of solubility was reached at about 1.75 grams per 100 c.c.

When a surface tension depression was observed, small additions usually exerted a relatively important influence, as is generally found with hydrosols. Thus, with potassium oleate and cellulose acetate in benzyl alcohol, it will be seen from Fig. 1 that beyond a concentration of about 6 grams of colloid per 100 c.c. of medium, the surface tension lowering effect becomes smaller.

Similarly, it was found that cellulose nitrate reduced the surface tension of amyl acetate at 25° by 4 per cent. with a concentration of 2 grams/100 c.c., and by increasing the concentration to 5 grams/100 c.c. there was only a further fall of 0.25 per cent.

Temperature Coefficient.—The temperature coefficient of the surface tension of sols could readily be obtained by the maximum bubble pressure apparatus recommended by Sugden. Some results obtained with sols in benzyl alcohol are shown in Fig. 2. A large number of readings were taken both with a rising and falling temperature; the points fell closely on the curves shown.

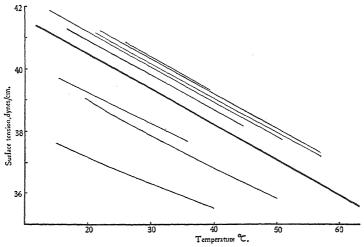


For sols of tannic acid, concentration 10 grams/100 c.c.; shellac 25/100; dragons blood 2.5/100; crystal violet dye 2.5/100; asphaltum 10/100; which had a slightly higher surface tension than the pure dispersion medium, the temperature coefficient was found to be practically the same as that of the solvent.

On the other hand, with potassium oleate  $2\cdot5/100$ ; colophony 50/100; and chlorophyll (oil soluble)  $2\cdot5/100$ , when the surface tension of the sol was below that of the dispersion medium, the lines relating surface tension and temperature tend to converge on that for benzyl alcohol at the higher temperatures.

Surface Tension and Temperature—With rise in temperature, the degree of dispersion of many colloidal substances increases; thus, the volume changes associated with the dispersion of cellulose acetate are larger at higher temperatures and there is less tendency for gelation.

Since the surface tension of the organosol is to some extent dependent on the degree of dispersion the change of surface tension of the sol with temperature should be different to some extent from the change for the pure dispersion medium. This might possibly explain the convergence of the surface tension—temperature curves for the sols on that for the pure dispersion medium with rise of temperature, there being an approach to a true solution.

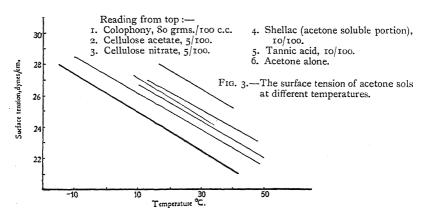


Reading from top:-

- 1. Asphaltum, 10 grms./100 c.c.
- 2. Tannic acid, 10/100.
- 3. Shellac, 25/100.
- 4. Dragon's blood, 2.5/100.
- 5. Crystal violet, 2.5/100.
- 6. Benzyl alcohol alone.
- 7. Potassium oleate, 2.5/100.
- 8. Colophony, 50/100.
- g. Chlorophyll, 2.5/100.

Fig. 2.—The surface tension of benzyl alcohol and sols at different temperatures.

Surface tension results obtained with various colloidal substances in acetone at different temperatures to — 10° C. are shown in Fig. 3. Cellulose acetate and also cellulose nitrate appear to have a much greater



effect in raising the surface tension of acetone than either tannic acid or shellac. The temperature coefficient of the surface tension of acetone and of the sols respectively are practically the same.

Results using formamide as dispersion medium are shown in Fig. 4. Formamide has a relatively high surface tension, and as in the case of

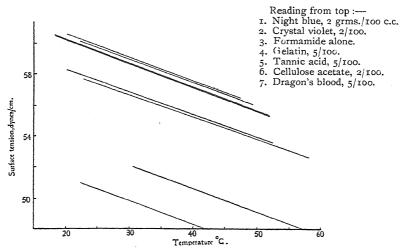


Fig. 4.—The surface tension of formamide and sols at different temperatures.

benzyl alcohol numerous instances of surface tension depression are found.

Similar temperature—surface tension relationships as those described above were obtained using acetic acid, benzene, alcohols, etc., for the dispersing medium. Some of these results are given later.

Behaviour of Colloids in Different Organic Liquids.—It may be observed from Figs. 2 and 4 that the surface tension of formamide is depressed by the addition of several colloids, which raise that of benzyl alcohol, although both the dispersing media have relatively high surface tension values. Thus, dragon's blood resin in concentration 5 grams/ 100 c.c. lowered the surface tension of formamide from 59.6 to 50.5 dynes/cm., yet the resin raised the surface tension of benzyl alcohol from 39.8 to 40.5.

Cellulose acetate, on the other hand, lowered the surface tension of both liquids whilst the dyes, night blue and crystal violet raised it; the dye rhodamine lowered the surface tension of formamide. So undoubtedly the relative specific characteristics of colloid and dispersion medium play an important part.

With liquids of low surface tension such as ethyl ether, acetone or the alcohols, the addition of colloidal substances was found to raise the tension or to exert little or no effect whilst with liquids of high surface tension a depression of surface tension usually occurred; this effect was most noticeable with water, formamide and aniline, and less so with benzyl alcohol, pyridine and benzene which have lower surface tensions.

From a consideration of this general behaviour it would appear that the colloidal solution can be compared with a mixture of liquids; a colloid would tend to lower the surface tensions of dispersion media greater than its own and raise those with surface tensions of less value.

The dyes, the potassium soaps and the heavy metal soaps, tannic acid, etc., raised the surface tension of methyl, ethyl and normal butyl alcohols. The surface tension of acetic acid was also raised by cellulose

acetate, dyes, resins, tannic acid, etc. Although most of the colloids raised the surface tension of benzene, yet copper oleate and chlorophyll lowered it very slightly. Tannic acid and colophony lowered the surface tension of pyridine appreciably although cellulose acetate raised it. Cellulose acetate, however, lowered the surface tension of aniline, benzyl alcohol, cyclohexanone and formamide. Cellulose nitrate lowered slightly the surface tension of amyl acetate.

Mixed Colloidal Substances.—When two sols with the same dispersing medium but containing different colloids were mixed in varying proportions the surface tension of the mixture differed only slightly, if at all, from the average value, any difference tending towards a lower surface tension. The following table gives a selection of the experimental data; the calculated values are included in brackets.

TABLE I.

	dynes  cm.		dynes/cm.
Formamide 25° C + dragons	59.4	Acetone 20° C, .	23.6
,, + dragons blood ,, + night blue.	50·7 59·9	,, + chlorophyll . ,, + colophony .	23·6 27·4
ı vol. dragons blood sol, ,, night blue sol .	54.9 (55.3)	Colophony sol $+$ 5 per cent, vol. chlorophyll sol.	26.2 (27.2)
o·5 vol. dragons blood soi, 3 vols. night blue sol .	58.6 (58.6)	${\tt I}$ vol. colophony sol ${\tt +}$ ${\tt I}$ vol. chlorophyll sol .	25.2 (25.5)
Benzyl alcohol 25° C	39 36·7 38	Benzene 20° C	28·9 28·1 31·5
,, + shellac ,, + colophony .	40·7 38·4	r vol. chlorophyl sol, r vol. colophony sol	28.8 (29.8)
ı vol. chlorophyll sol, ,, cellulose acetate sol	37.4 (37.35)	<pre>vol. chlorophyll sol, vols. colophony sol .</pre>	29.7 (30.6)
ı vol. shellac sol, ,, colophony sol .	37·3 (39·6)	Acetic acid 25° C , + gelatin , + cellulose acetate	25·7 24·8 28·5
Shellac sol + 10 per cent. colophony sol	38.8 (40.5)	vol. gelatin sol, ,, cellulose acetate sol	26.5 (26.7)
Shellac sol $+$ 10 per cent. cellulose acetate sol .	38.6 (40.4)	Ethyl alcohol 25° C. ,, + chlorophyll ,, + shellac .	21·9 22 24·3
I vol. cellulose acetate sol, ,, colophony sol .	36.9 (38.2)	I vol. chlorophyll sol, 3 vols. shellac sol	23.5 (23.7)
2 vols. cellulose acetate sol, 1 vol. colophony sol .	36.8 (38.1)	ı vol. chlorophyll, ,, shellac	23.1 (23.2)

Colloids in Mixed Liquids.—The composition of a binary mixture has a profound influence on the properties of a sol; thus, the viscosity, degree of dispersion, clarity and gelation temperatures of a cellulose

ester sol in ether-alcohol mixtures or ester-alcohol mixtures vary over a wide range with composition, the pure liquids often not being solvents.

It has been found possible in some instances to correlate the degree of dispersion with the effect of the colloid on the surface tension; thus, with cellulose acetate in cyclohexanone-benzyl alcohol mixtures the depression effect is least with the best solvent mixture, there being least colloidality.

A reverse effect was found with acetone-phenol or aniline-phenol mixtures when complex formation occurring between the different molecules of the binary mixture results in a fall of solvent power and consequently an increase in the surface tension depression. This correlation is shown graphically in Fig. 5 which gives the relationship between drop volume and solvent power for different mixtures.

With cellulose nitrate in ether-alcohol mixtures when the surface tension of the dispersing medium is low there was found a slight increase

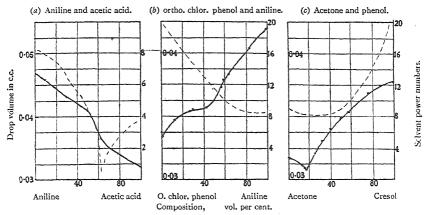


Fig. 5.—Surface tension measurements of cellulose acetate in binary mixtures of liquids; correlated with solvent action. (Chain lines—solvent power numbers—J.C.S., 125, 2244, 1924.)

in surface tension and the increase varied but little with the composition of the mixture.

When acetone, alcohol or ether is added to water the surface tension depression effect of the colloid rapidly decreases with increase in amount of the added organic liquid until the sol has the same or greater surface tension than the pure dispersion medium. Thus, I per cent. potassium oleate in equal volumes of water and acetone raised the surface tension by 0.6 dynes/cm. Similarly in ethyl ether saturated with water the soap raised the tension appreciably.

In the following Table II. (Fig. 6) are given the surface tension data for gelatin, tannic acid, cellulose nitrate, and night blue in mixtures of acetic acid and water and in mixtures of alcohol and water at 25° C. When the amount of water in the binary mixture falls below 75 per cent. the surface tension depression practically disappears and with further decreases there is a tendency for the surface tension curve of the sol to cross that of the pure liquids.

This is seen especially in the case of gelatin in water-ethyl alcohol mixtures; the curves cross at the point for 85 per cent. water.

TABLE II.

(a) The surface tension of sols of gelatin, tannic acid, etc., in mixtures of acetic acid and water at 25° C.: dynes/cm.

Composition of Dispersing Medium. Weight Per Cent. Acetic Acid.	Dispersing Medium.	Gelatin, 2/100.	Tannic Acid,	Night Blue, 1/100.	Cellulose Acetate, 2/100.
o (water) 8.4 22.2 48.3 78.8 85.3 89.8 Glacial acetic acid.	72·2 55·7 45·85 39·64 33·2 31·5 30·3 25·7	58·2 48·8 45·8 39·61 33·2 31·5 30·2 24·9	63.8 55.7 45.9 39.7 33.4 31.7 30.4 26.3	67·9 45·85 — — 30·3	33·5 31·2 26·7

# (b) The surface tension of sols in mixtures of ethyl alcohol and water at 25° C.

Composition of Dispersing Medium. Weight Per Cent. Ethyl Alcohol.	Dispersing Medium.	Gelatin, 2/100.	Tannic Acid, 10/100.	Night Blue, 1/100.
10 20 33 40·6	47·1 38·9 31·4 29·6	44·2 36·1 31·3	46·3 39·0 — 30·9	47°I — —

### (c) The surface tension of sols in mixtures of water and glycerol.

Glycerol-water Mixture of Density 1'2213	Glycerol-water Mixture of Density 1'1292	
at 15° C.	at 15° C.	
Dispersion medium, 40° C — 64·2	Dispersion medium, 30° C — 67·3	
Gelatin sol 2/100, 40° C — 64·25	Gelatin sol 2/100, 30° C — 59·7	
Tannic acid sol 10/100, 40° C. — 64·35	Tannic acid sol 10/100, 30° C. — 62·2	

Bircumshaw considered that since potassium oleate forms practically non-associated solutions in ethyl alcohol the transition from the surface lowering to surface raising effect could be explained on this basis. The simpler explanation appears to be preferable, namely that most substances raise the surface tension of ethyl alcohol and other organic liquids of low surface tension but lower that of water of high surface tension. Undoubtedly the degree of colloidality or degree of dispersion is influenced by variations in the composition of the binary mixture; this is indicated by the behaviour of gelatin in water mixtures. An addition of a quarter volume of acetic acid to a hydrosol of gelatin favours the solvent action, the gelatin temperature being reduced considerably, whilst on the other hand a quarter volume of ethyl alcohol makes little difference and it can be noticed from Fig. 6 that the increased solvent action by the acetic acid addition is accompanied by a relatively large fall in surface tension lowering effect.

**Frothing.**—Although considerable frothing was observed with many of those sols which had a surface tension below that of the pure dispersion medium, *e.g.*, cellulose acetate or dragon's blood in formamide,

chlorophyll in benzyl alcohol, copper oleate in benzene, etc., yet there appeared to be no relation between the amount of frothing and the amount of the depression in surface tension. The sols of colophony and cellulose acetate in benzyl alcohol frothed only slightly although a lowering of

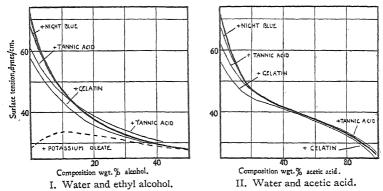


Fig. 6.—The surface tension of I. Water-ethyl alcohol mixtures and sols, II. Water-acetic acid mixtures and sols, 25° C. Chain-line—Potassium oleate (Bircumshaw).

the surface tension had occurred. Frothing was also found with some organosols which had a surface tension greater than that of the dispersion medium, e.g., tannic acid in acetone or acetic acid, shellac in alcohol, mastic gum in ether, etc.

## Summary.

I. Surface tension measurements with numerous organosols have been made at different temperatures and concentrations by means of the drop-weight and maximum bubble pressure methods. The general behaviour of the colloids was to lower the surface tension of liquids with high surface tension, e.g., formamide, benzyl alcohol, aniline, etc., and to raise the surface tension of liquids of low surface tension such as ethyl ether, ethyl alcohol or acetone. In this behaviour the colloids resemble many crystalloids.

2. The surface tension of colloids in mixed liquids was dependent to a large extent upon the values obtained with the single solvents, but the influence of the specific character of the substances used and the variation in solvent action with composition could be clearly traced in many instances. Increased solvent action with its concomitant fall in colloidality resulted in a fall of the surface tension lowering effect.

3. Mixed colloids in single liquids had a surface tension the same or

slightly lower than the calculated value.

4. No correlation could be made between frothing and surface tension.

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#### AN INVESTIGATION OF THE GLOW OF PHOSPHORUS WITH THE AID OF PHOTO-ELECTRIC COUNTER.

By C. Ouellet (communicated by E. K. Rideal).

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It is well known that phosphorus vapour and oxygen react only within certain limits of pressure—the explosive limits. Lord Rayleigh 1 showed the absence of luminescence above a critical limit, although a very slow reaction was observed, whilst Semenoff 2 demonstrated the existence of the lower critical pressure, and showed that it was given by the expression:

$$P_{O_2} P_{P_4} \left( \mathbf{I} + \frac{P_A}{P_{O_2} + P_{P_4}} \right) d^2 = K$$
 . (1)

where the partial pressures of oxygen and phosphorus are  $P_{O_2}$  and  $P_{P_4}$ respectively;  $P_A$  the partial pressure of a neutral gas, and d the diameter of the reaction vessel. From the early work of Centnerszwer 3 and Ewan 4 there is no reason to suppose that this system differs from that of hydrogen and oxygen.<sup>5</sup> The exact origin of the luminescence, however, is not yet perfectly known. The fact that no glow can be seen outside the region where chain propagation occurs, and, furthermore, the close similarity between the spectra produced by the oxidation of phosphorus vapour, phosphine and phosphorus oxide 6 makes it appear likely that the luminescence is associated with the presence of secondary centres which multiply through collision of an active product or link in the chain with other oxygen molecules. Ordinary methods of observation seem to be of little value in ascertaining whether any radiation is emitted in the absence of chains. It was thought desirable, however, by means of a Geiger Müller tube type counter 7 to investigate the kinetics of the oxidation of phosphorus in the region of luminous glow as well as in those regions in which no such glow can be observed, by determination of the rate of emission of quanta of radiation to which the quantum counter responded. The quantum counter was constructed of a quartz tube 5 cms. long with internal and external diameters of 1.5 and 1.65 cms. respectively, coated on the inside with a thin film of platinum acting as the photo-electric emitter. A thin uniform tungsten wire was stretched by means of good ebonite bushes along the axis of the tube; after the bushes had been sealed in with picene wax, clean, dry and dust-free air was admitted to a pressure of 4-7 cms. Hg. The wire was connected to the earthed positive terminal of a 1200-1500 volt high-tension battery

<sup>&</sup>lt;sup>1</sup> P.R.S., 106A., 1, 1924. <sup>2</sup> Z. Physik, 46, 109, 1927. <sup>3</sup> Z. physik. Chem., 26, 1, 1898; 85, 99, 1913.

<sup>5</sup> See Semenoff, loc. cit.; Z. physik. Chem., 2B., 161, 1929; Dalton and Hinshelwood, P.R.S., 125A., 294, 1929.

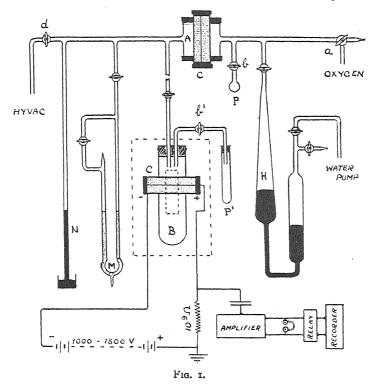
<sup>6</sup> Emeléus, J.C.S., 127, 1362, 1925; 788, 1927.

<sup>7</sup> Geiger and Müller, Naturwiss., 16, 617, 1928; Physik. Z., 29, 839, 1928;

<sup>36, 489, 1927;</sup> Rajewski, Z. Physik, 63, 1930; Physikal. Z., 32, 121, 1931.

mounted on wax through a 10° ohm resistance, as shown in Fig. 1, and through a condenser to the grid of a Loewe three-stage amplifying valve. The anode current of the valve operated a high-speed post-office relay which, in turn, controlled the operation of a mechanical recorder of the standard telephone type.

In operation a photo-electron emitted from the metal film is accelerated by the field and owing to multiplication of ions by collision ultimately gives rise to a discharge accompanied by a drop of potential which reacts on the grid of the amplifying valve. The discharge ceases automatically, and after a period of the order of 10<sup>-3</sup> seconds the potential returns to its initial value and the surface properties of the electrodes disturbed by the discharge recover their normal state. Such a counter possesses a



high sensitivity. The upper limit of intensity is controlled by the size of the counter and the period of recovery of the electrodes and electrical system. In normal operation these counters recorded 10-15 times per minute, a residual effect largely due to the cosmic rays; these served as control for the proper functioning of the electrical system.

The threshold of the radiation to which the counter was sensitive was investigated by means of a quartz monochromator and iron arc and found to lie around  $\lambda = 2800$  Å.

The order of the sensitivity was estimated by comparison with a thermopile, using the radiation from a quartz mercury lamp. The total energy radiated by the lamp on I sq. cm. at I metre distance was measured with the thermopile. The lamp was then placed at 5 metres

from the counter, behind a slit letting through only 10 per cent. of the light. A further reduction of  $8 \times 10^{-5}$  was obtained by placing in front of the counter a very fine slit, which was calibrated with a weak source, and a quartz lens of 4.7 cm. focal length at a distance of 57 cm. Assuming that some 10 per cent. of the total radiation lies in the spectral region to which the counter is sensitive, the effective intensity was  $3.7 \times 10^{-8}$  erg./cm.²/sec. or  $5 \times 10^3$  quanta of  $\lambda = 2500$  Å, and the resultant increase in the number of impulses was found to be 50 per minute. As, by counting up to some 5000, an increase 100 times smaller can be detected, it follows that the limit of sensitivity reached in some of the following experiments was of the order of 50 quanta per sq. cm. per second, to be compared with that of 10  $h\nu$ /cm.²/sec. obtained by Rajewski (loc. cit.?).

# Apparatus.

Electrolytic oxygen dried by phosphoric anhydride is admitted through  $\alpha$  (Fig. 1) to the reaction vessel A or B and pieces of clean dry white phosphorus placed in the containers  $P_1P^1$ . The reaction vessel A for use at low pressures was built round the counter C with an annular separation of 3 mm. corresponding to a lower explosion pressure of 0·3 mm. Hg; all tube connections were of less than 3 mm. bore. The oxygen pressure in A could be adjusted by means of the conical compressor H, which pressure was read by means of a microscope on the sulphuric acid manometer M. The reaction vessel B designed for use at high pressures, where the size of the vessel does not affect the reaction, consisted simply of a glass tube 13 cm. by 4 cm. through which the counter was sealed, the whole vessel being introduced into a light tight box painted black; the pressures being read on the manometer.

# The Upper Limit of Reaction.

The reaction vessel B was filled with oxygen at atmospheric pressure and phosphorus vapour allowed to diffuse in from P¹. The pressure was then gradually reduced and the flash-point determined; the same process was then repeated and the pressure lowered to a value slightly above the flash-point. The number of impulses given by the counter were then recorded, alternating with control runs when the reacting system B was either evacuated or filled with oxygen at atmospheric pressure. With pure oxygen the flash-point was found to be at 595 mm. pressure and in oxygen containing some nitrogen the flash-point was 400 mm. The results obtained with the counter at the higher pressures are summarised in the table on opposite page.

The limits of statistical error are indicated in each series. It will be observed that above the critical pressure no radiation of wave-length less than 2800 Å. is detectable down to an intensity corresponding to I per

cent, of the residual effect due to cosmic rays.

#### The Lower Limit of Reaction.

The experiments to determine the lower limit were conducted by evacuating A and allowing phosphorus to diffuse into the vessel. Oxygen was then gradually admitted either through the dosing tap a or by means of the compressor H. The critical pressure was found to be 0.3 mm. Hg as read on the gauge M. A series of short runs at pressures below

TABLE I.

1	Reaction. Flash Limit 595 mm. H	Ig.	Cont	rol.
Pressure in mm. Hg.	Time in Minutes.	Number of Impulses.	Time in Minutes.	Number of Impulses.
600 610 620 650 710	60 50 60 130 90 —	1004 920 994 2002 1426 6346 ± 80	90 90 60 90 60 —	1420 1652 965 1452 930 6419 ± 80

Reaction. Flash Limit 400 mm. Hg.			Control.
Mean of 40 Runs at	Time in Minutes.	Number of	Number of
Pressures 400-760 mm.		Impulses.	Impulses.
	120	2204 ± 47	2160 ± 47
	78	1419 ± 37	1400 ± 37

0.3 mm. were carried out, including longer runs at 0.25 mm. Hg; the data recorded below indicate no emission of radiation.

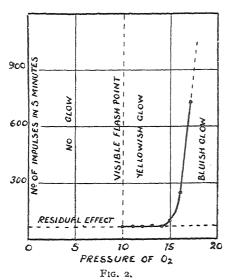
Time in	Impulses Recorded.		
Minutes.	In Reaction.	In Control.	
Total of short runs 70	636	618	
Total of long runs 270	3961	3965	
	4597 ± 68	4538 ± 68	

#### Examination of the Glow.

If the pressure of oxygen in A is brought slightly above the lower limit of pressure and the tap to the phosphorus container P left open, a faint pulsating yellowish glow could be observed in the dark, due to the slow diffusion of phosphorus vapour into A. This glow had no effect on the counter. At higher pressures the colour changes to a more bluishgreen tint without noticeable change in intensity, and radiation affecting the counter is emitted. The dependence of the rate of liberation of quanta on the oxygen pressure in this range of pressures is shown in Fig. 2, the pressures being given in arbitrary units.

This behaviour was more noticeable in reaction vessel B, although the critical pressure was much lower, ca. 1.5 10<sup>-3</sup> Hg.

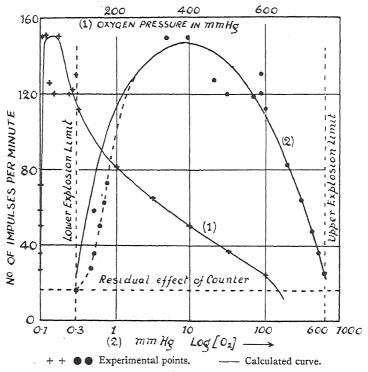
In order to follow the variations in the intensity of the glow with the



oxygen pressure, a tiny piece of phosphorus was introduced into the vessel A and left to react until the formation of protective layers on the phosphorus and on the walls had sufficiently reduced the rate of reaction and the sensitivity of the counter. In spite of the severe stress exerted upon the counter by the periodical flashes the changes in the luminosity of the background could be followed.

The results obtained are shown graphically in Fig. 3, where the pressures of oxygen are plotted both on a normal and a logarithmic scale against the number of impulses per minute recorded by the counter.

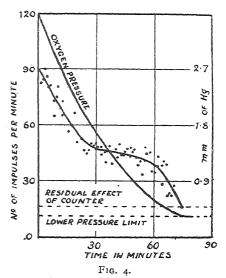
The dependence of the glow upon the rate of reaction as measured



F1G. 3.

by the change of oxygen pressure with the time is shown in Fig. 4, where it is seen that the number of impulses is not proportional to  $-\frac{dp}{dt}$ , the rate of the decrease of the pressure, but reaches a more or less constant level and then drops abruptly as the lower pressure limit is approached.

The form of the curve depicted in Fig. 3 can readily be accounted for on the hypothesis of a chain mechanism of the type proposed by Semenoff. we assume that the active centres are oxygen atoms, then we obtain the following possible sequence of reactions:-



I. 
$$O + P_4 \rightarrow P_4O^1 \left\{ \begin{array}{l} P_4O^1 + O_2 \rightarrow P_4O + O + O \\ P_4O^1 + P_4 \rightarrow P_4O + P_4 \end{array} \right.$$
 (a)

4. 
$$P_4O_4 + O_2 \rightarrow P_4O_6^1$$

5. 
$$P_4O_8 + O_2 \rightarrow P_4O_{10}^1 \begin{cases} P_4O_{10}^1 + O_2 \rightarrow P_4O_{10} + O + O \\ P_4O_{10}^1 + P_4 \rightarrow P_4O_{10} + P_4 \end{cases}$$
 (a)

To which we may add a process of the type:

6. 
$$P_4O_{10}^1 \rightarrow P_4O_{10} + h\nu$$
,

the deactivation taking place spontaneously with emission of the excess energy.

In the presence of excess oxygen we may also assume that deactivation of the centres, the oxygen atoms produced by the reactions (a) cited above, proceeds 8 according to:-

7. 
$$O + O_2 + O_2 \rightarrow O_3^{\ 1} + O_2^{\ 1}$$
  $O_3^{\ 1} + O_2 \rightarrow O_3 + O_2$   
8.  $O + O + O_2 \rightarrow O_2^{\ 1} + O_2^{\ 1}$   $O_2^{\ 1} + O_2 \rightarrow 2O_2$ 

The luminescence produced during the oxidation taking place in the gaseous phase is governed by (6), which in turn is controlled by :-

- (a) The rate of evaporation of the solid phosphorus.
- (b) The breaking of the chains by collision between the links, (7), (8).
- (c) The quenching of the luminescence by oxygen and phosphorus molecules, (5) (a) and (b).

We may consider that the number of chains initiated in unit time is proportional to the rate of supply of P4 molecules by evaporation,

where  $P_0$  is the vapour pressure of phosphorus.

P = actual pressure of phosphorus in the gaseous phase.

8 See Harteck and Kopsch (Z. physik. Chem., 12B, 333, 1931).

From Semenoff's equation the actual pressure of  $P_4$  is given by:—

$$[P_4][O_2] = K_2$$
, or  $P = [P_4] = \frac{K_2}{[O_2]}$ .

In the present case  $P_0=0.035$  mm. Hg and the lower limit of pressure of the oxygen is 0.3 mm. Hg, so that  $K_2\cong 10^{-2}$ . Equation 1.1 then becomes:-

$$\frac{dx}{dt} = K_1 \left( 0.035 - \frac{10^{-2}}{\left[ O_2 \right]} \right), \qquad . \qquad . \qquad . \qquad 1.2$$

where [O<sub>2</sub>] is expressed in mm. Hg.

The active centres [0] can, as we note, give rise to two processes: formation and propagation of chains by reaction with molecules of phosphorus (1) or breaking of chains by reacting according to (7) or (8), the rate of which is proportional to  $[O_2]^2$ , the number of triple collisions increasing as the square of the pressure; then the probability of the extension of the chain will be:-

This expression decreases rapidly as the upper explosion pressure is reached, the propagation of the chains becomes more difficult as deactivation increases, until it ultimately stops.

We have assumed that the radiation is emitted by the spontaneous deactivation of an active produce such as P<sub>4</sub>O<sub>10</sub><sup>1</sup>. There are three competing processes involved in the ultimate fate of this species :-

Whilst the emission of radiation is due to (6), deactivation without emission of radiation is effected by (5a) and (5b). If X be the total number of  $P_4O_{10}^{-1}$  molecules deactivated per second, and  $X_{5a}$ ,  $X_{5b}$ ,  $X_6$  the numbers deactivated according to the above reactions, we obtain:

$$X = X_{5a} + X_{5b} + X_6$$
 . . . 1.4

and from (5a) and (5b):

$$\frac{X_{5a}}{X_6} = \beta(O_2) \qquad \frac{X_{5b}}{X_6} = \gamma(P_4).$$

Inserting in 1.4 these values of  $X_{5a}$  and  $X_{5b}$  we obtain:

$$X = X_6 \{ 1 + \beta(O_2) + \gamma(P_4) \}.$$

It is permissible to call  $\gamma(P_4)$  zero, since the stationary pressure of phosphorus is exceedingly small.

Whence, 
$$X_6 = \frac{X}{1 + \beta \lceil O_9 \rceil}.$$
 . . . . . . . 1.5

Inserting in the general equation for the rate of emission of radiation involving the three factors a, b, c, we obtain:—

$$N - N_0 = K \text{ (I·I) (I·3) (I·5)},$$

or the number of impulses per minute in the counter is given by :-

$$N-N_0=K\times \Big(P_0-\frac{k}{[\mathrm{O_2}]}\Big)(\mathrm{I}-\alpha[\mathrm{O_2}]^2)\,\Big\{\frac{\mathrm{I}}{\mathrm{I}+\beta[\mathrm{O_2}]}\Big\},\quad \mathrm{I}\cdot\delta(\mathrm{O_2})^2=0$$

where  $N_0$  is the number of impulses per minute due to extraneous sources such as the cosmic rays.

By analysis of the decreasing branch of curve I into two components, values were assigned to  $\alpha$  and  $\beta$ .

If at the highest rate of reaction it is assumed that no inhibition occurs and that  $P_0$  and k are derived from the vapour pressure curve and Semenoff's equation respectively, we then obtain for 1.6:—

$$N-N_0 = {\rm i} 35 \Big(0.035 - \frac{{\rm i} 0^{-2}}{[{\rm O_2}]} \Big) ({\rm i} - 2.{\rm i} 0^{-6} \, [{\rm O_2}]) \Big\{ \frac{{\rm i}}{{\rm i} + 4.\, {\rm i} 0^{-3} \, [{\rm O_2}]} \Big\}.$$

The plot of the curve in which the only two arbitrary constants are  $\alpha$  and  $\beta$  derived from this equation is given in Fig. 3 with the experimental values, and a few of the calculated and observed rates are given in Table II. The agreement is remarkably good.

It appears that up to the sensitivity obtained with these quantum counters no radiation is emitted outside the region where chain propagation occurs, supporting the assumption that the glow is emitted only during the secondary stages of the reaction and possibly during the oxidation of  $P_4O_6$  to  $P_2O_5$ .

Furthermore, it appears from the results shown in Fig. 2 that the various spectral

TABLE II.

[O <sub>2</sub> ] in mm. Hg.	$N - N_0$ Calc.	$N-N_0$ Obs.
75	104	102
100	94	95
200	94 69	66
300	50	50
400	32	32
500	21	21
600	9	9

components of the glow are not rigidly bound to each other but may vary independently, as already observed by Emeléus 6 in the case of the band at  $\lambda=3270$  Å. Some or all of the bands situated above  $\lambda=2800$  Å., the threshold value of the counter, are emitted only or suddenly increase in intensity at a pressure which is definite and higher than that at which the visible glow sets in. It is possible that there exist two chemical reactions involved as components constituting the glow unequally affected by pressure, a suggestion supported by the form of the intensity time curve (Fig. 4) which could be analysed as the sum of the intensities of two individual radiations emitted by two subsequent processes.

#### Summary.

The construction of a sensitive photo-electric counter is described and the kinetics of the oxidation of phosphorus examined with its aid. It is shown that no radiation of wave-length < 2800 Å. is emitted outside the explosive limits as defined by Rayleigh and Semenoff. The effect of change in pressure of the oxygen on the glow of phosphorus is examined and the variation in intensity of the radiation emitted is shown to follow that anticipated from a chain mechanism of a type proposed by Semenoff. The glow is shown to be composite and it is suggested that two chemical reactions in sequence unequally affected by the gas pressure are involved.

My thanks are due to Professor E. K. Rideal, F.R.S., for suggesting the investigation; to him and to Dr. O. H. Wansbrough-Jones and Dr. G. Occhialini for assistance and advice during the progress of the work, and to the Government of the Province of Quebec, Canada, for a research Fellowship.

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## THE MECHANICS OF GELATION.

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In the setting of a gel, the change from a liquid to a semi-solid possessing a structure is accompanied by changes in a number of its properties. Perhaps it is more usual to observe the transformation by the onset of turbidity in the Tyndall cone, but not the least instructive changes are those which take place in the viscosity and elasticity of the substance. The former quantity is usually measured in a flow tube or concentric cylinder apparatus. The increase in viscosity with time until gelation sets in was observed seventy years ago by Graham 1 in silicic acid, while Levites 2 has made extensive measurements of the decrease in outflow of a gelatine solution from a reservoir with lapse of time. The elasticity of a sol has been measured by Schwedoff,3 and later by Hatschek and Jane.<sup>4</sup> The method involved the use of a cylinder suspended in the sol. The upper end of the suspension wire is twisted, and the cylinder follows through a smaller angle. The experiments to be described aim at an examination of these properties of gelating sols in a rather more "fundamental" method than that of the concentric cylinder apparatus as generally used.

It is perhaps not generally realised what a useful piece of apparatus for the *simultaneous* study of both viscosity and elasticity is afforded by the oscillating disc apparatus used by Meyer <sup>5</sup> for studying the viscosity of homogeneous liquids. Meyer obtained a formula for the viscosity of the liquid, involving, beside the dimensions of the apparatus, the decrement and the time-period of the oscillations. As a matter of fact, the former depends on the damping, *i.e.*, the viscosity of the liquid plus the very small friction in the suspension, while the time-period is mainly a function of the elasticity of the liquid and of the inertia and elasticity of disc and suspension wire, since damping has a second order effect on the period. From measurements of the decrement and time-period of the oscillating disc at intervals while the gelation is taking place, we can study the relative changes in viscosity and in elasticity respectively.

<sup>&</sup>lt;sup>1</sup> Trans. Chem. Soc., 618, 1864.

<sup>2</sup> Kolloid. Z., 2, 210, 1907.

<sup>&</sup>lt;sup>3</sup> J. Physique, 8, 341, 1889. <sup>4</sup> Hatschek and Jane, Kolloid. Z., 39, 300, 1926. <sup>5</sup> Ann. Physik, 113, 85, 1861.

Writing the equation of the oscillating system in the form

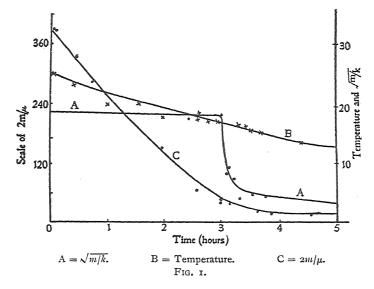
$$m\frac{d^2y}{dt^2} + ky + \mu\frac{dy}{dt} = 0,$$

where m represents the effective inertia of the disc, including the additional load due to any structural binding to the gel, k represents the elastic and  $\mu$  the viscous force; the solution is of the form

$$y = ae^{-\alpha t} \sin \omega t$$

where  $\alpha$  (the damping coefficient) =  $\mu/2m$ , and  $\omega(=2\pi \times \text{frequency of oscillation}) = \sqrt{k/m - \mu/4m^2}$ .

Thus when the damping is small the square of the frequency is a measure of k/m, while the rate of decay of amplitude is a measure of  $\mu/m$ . To a first approximation, then, observations of the increase in



frequency will exhibit the gradual acquirement of elastic properties, while observations of the times taken to fall through a given range of amplitude will indicate the corresponding changes in viscous properties, while the gel sets.

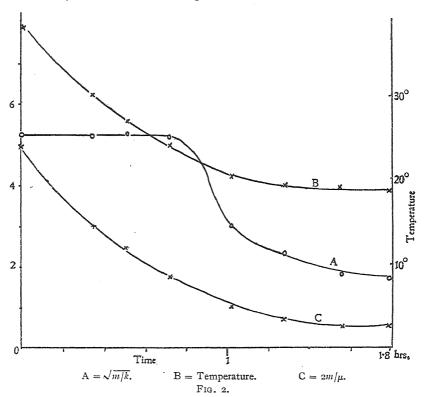
Actually, in the next three figures it is the reciprocal of the time to fall to 1/e of the original amplitude which gives  $\alpha$  and  $\sqrt{4\pi^2/T^2 + \alpha^2}$  (T being the measured time-period), which gives  $\omega$ . Both quantities k/m and  $\mu/2m$  are properties of the oscillating system together with the circumambient fluid, but measurements of time-period and decrement in air alone indicate that it is the fluid which exerts the predominating influence.

Fig. I shows results with an oscillating disc in a I per cent. gelatine solution. It will be noticed that the damping increases gradually, but not enough to affect the time-period, which remains constant until (at 18·2° C.) there is a sudden drop in time-period as the gel sets. Meanwhile the increase in viscous drag goes on gradually but less rapidly.

Fig. 2 shows a type (1 per cent. agar) in which the setting produces a very stiff gel, as shown by the large change in time-period, which is

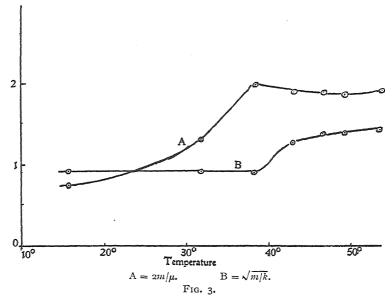
accompanied by a gradual change in the decrement.

Fig. 3 shows results for a peculiar gel discovered by Szegvari, made by dissolving nitro-cellulose in amyl acetate and thinning with benzene. As this mixture is warmed it becomes less viscous, but at about 50° C. the nitro-cellulose disperses in the benzene to form a gel. We see on the figure the continuous diminution of viscosity as the mixture is heated to the gelating temperature, when again the sudden change of time-period is evident, without further change in decrement.



We conclude, then, from these graphs that increase in viscosity per se is not the dominant factor in determining gelation. In confirmation of this aspect, an experiment in thixotropy, the inhibition of gelation by mechanical agitation, was set up. A dipper at the free end of an electromagnetically maintained reed was kept working at the surface of some of the hot gelatine solution placed in a developing dish, in the same fashion as for the familiar laboratory demonstrations in the ripple tank. The light falling from a stroboscope on the surface of the liquid at a fixed oblique angle, measurements were made from time to time of the distance from the dipper to which the crests of the waves could be distinguished as the solution cooled. This distance is evidently inversely proportional to the viscosity of the liquid, provided the amplitude of the

vibration is maintained constant. (Thus, if the amplitude of a crest it  $a_0e^{-\alpha x}$ , and if the just visible amplitude given by  $a=a_0e^{-\alpha x_1}$  is found at a distance  $x_1$  from the source,  $\alpha x_1=\log a_0/a=$  constant, where  $\alpha$  is the coefficient of viscous damping. It is assumed that the wave-length is sufficiently small compared to the width of the dipper to prevens lateral spreading of the waves.) The results are shown in the following table. The viscosity continually increases, as is natural, but it will be



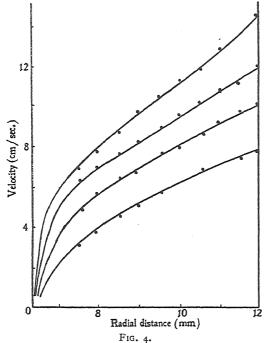
noticed that the solution remains liquid after it has passed the normal gelation point (18° C.)—shown by an undisturbed control solution—down to 10° C., at which temperature it suddenly sets, and the capillary waves disappear. Evidently, then, some structural change in the gel is inhibited by the agitation, but this does not affect the usual viscosity increase.

Distance reached by Waves (cm.). Temp. Relative Viscosity. Remarks. 20° I Sol. 180 6 1.3 16° 5 1.6 2 4 140 3 2.6 13.5° 2.6 Thixotropic gel. 3 12·5° 4 2 11º I 100 Normal gel.

TABLE I .- VISCOSITY OF A THIXOTROPIC GEL.

It was found that similar thixotropic effects could be reproduced in gels by using the supersonic agitation of a gelating sol caused by a piezo-electric quartz oscillator exposed to the fluid.

The difficulty in applying the results of such graphs as these lies in the fact that the viscosity of a colloid varies with the shear applied to it as well as with the time. Thus, although such measurements exhibit qualitatively the changes which accompany gelation, the fact that the speed of the disc and, therefore, the rate of shear varies during each oscillation prevents an accurate analysis of the changes of viscosity and rigidity which occur. For the suspensoids, the variation of viscosity with velocity gradient has already been determined by Dr. E. Tyler and the author, using a concentric cylinder apparatus provided with a hotwire anemometer. It was found difficult to get a plot of velocities in gelatine with this apparatus owing to the change of viscosity which takes



place during a series of readings, during which the liquid was subjected to shearing forces for five minutes at least.

Fig. 4 shows one of the more successful plots of velocity between the two cylinders, of which the outer rotates and the inner is still. If the viscosity had the normal, velocity distribution would have been nearly a straight line, instead of which the velocity falls steeply to the surface of the inner cylinder.

In order to get more detailed data of the behaviour of the gelatine to shearing forces during the process of gelation, the revolving disc apparatus was modified in the following manner. The suspension wire was

removed and the vertical axis set in ball bearings. On a continuation of this axis a small wooden pulley was mounted, set with pins round half of its circumference. The light from a Pointolite lamp passing through a horizontal slit cast a shadow of these pins on the film of a moving-film camera. A shear was applied to the liquid by a weight at the end of a thread passing round the pulley and over a nearby vertical pulley. When the weight had fallen a short distance it was removed by a tripping device. At the same instant the film in the camera was set in motion until all movement of the disc had ceased. The slit through which the exposing light passed was made up of two aluminium vanes attached to the prongs of a Tinsley standard tuning fork. Consequently, twenty-five exposures per second were made on the film, and against the background of these interruptions, the shadows of the pins moved to-and-fro.

From these films, exposed at intervals, the damping and elasticity factors

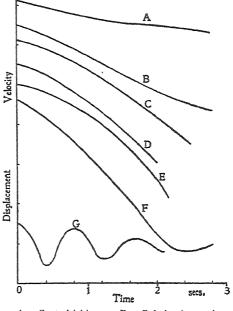
were calculated, before and during the setting of the gel. A "control" film to allow for the damping of the bearings was made in air alone at the conclusion of the series. Results in the form of velocity against time are shown in Fig. 5.

The points to be noted in these curves are:

 The increase in average damping during the period covered by the results.

(2) The growth of rigidity; first apparent as a slight return movement of the disc at the end of its run, and afterwards as a rapid to-and-fro movement. The frequency of this oscillation is still growing long after the jelly has apparently set.

(3) A variation of damping with speed of disc—the extent of variation increasing until setting

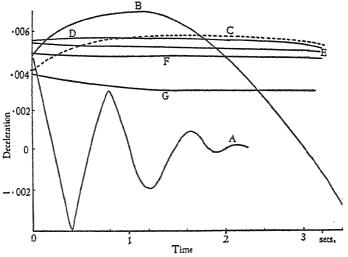


A = Control (air).
C = After 2 hrs.
E = After 6 hrs.
G = After 10 hrs.

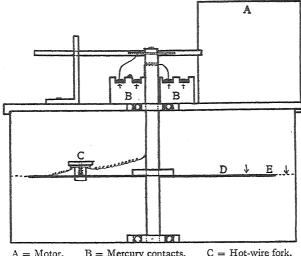
B = Gelatine (at start). D = After 4 hrs.F = After 8 hrs.

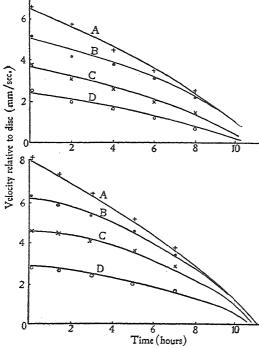
Fig. 5.

takes place. Just before this, the substance seems in an unstable



A = Air. B = Start. C = 2 hrs. D = 4 hrs. E = 6 hrs. F = 8 hrs. G = 10 hrs. Fig. 6.





A = Disc velocity = 15 mm./sec. B = 11 mm./sec. C = 7.5 mm./sec. D = 5.5 mm./sec.

Top diagram at 1 mm. distant from disc. Lower diagram at 1.5 mm. distant from disc.

Fig. 8.

state; it is disturbed out of its rigidity and viscosity by the applied shear, but recovers as the disc slows down.

Fig. 6 gives more striking details about the development of anomalous viscosity and rigidity. Here the celerations are plotted a t various hours after making the sol, the data being ob-

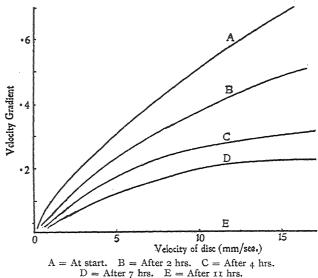
tained from the last figure (5). At first the disc comes to rest under a nearly constant damping force, but after some hours there is a notable diminution of damping force at both ends of the motion, while at eight hours the curve has become definitely sinusoidal, and at ten hours rigid damped oscillation takes place.

In order to get more detailed information on mechanism, velocity gradient in close proximity to the disc in rotation was examined by a hot wire anemometer. The disc was kept rotating at constant speed by a small motor, mounted on the tank cover, which drove the former through a worm gear. The hot of nickel was (.001-inch diameter), soldered to two needles. forming a little fork which could be moved up and down by a micrometer head mounted on the upper side of the disc. Electrical contact was assured by two fixed mercury "rings" on the cover, into which rings there dipped leads passing up the axle from the fork. Fig. 7 shows the apparatus as adapted for measurements of velocity gradient.

The speeds used were sufficiently slow to warrant an assumption of stream-line motion of the fluid with negligible radial flow. In use, the surface of the liquid was just flush with the disc; but, in the calibration of the hot wire for velocity measurements in terms of its electrical resistance, the liquid surface was kept I cm. below the disc. A correction

was made for the drift induced by the rotating axle while the calibration curve was being ob-The tained. inside of the containing vessel was greased to the prevent adhering gel to it.

Results in the form of velocities relative to the disc in gelatine at different epochs during gelation are presented for



distances from the surface of the disc of I mm. and I·5 mm. respectively, and for four different speeds of the disc in the succeeding Fig. 8; Fig. 9 shows the same results plotted in the form velocity gradient: velocity of disc. In the absence of radial flow these should be straight lines if Newton's law holds. Actually the initial one is nearly so, but as time elapses the anomalous viscosity characteristic of colloids sets in, until eventually the gel sets throughout. It may be mentioned that the velocity gradients in the last stages of gelation were very difficult to get. Just before complete setting, the mass would move as a more or less rigid whole with the disc, but after a few revolutions a sudden relaxation would occur, often tearing away the hot wire. At other times, the gel would set round the wire prematurely. For these reasons few results in the final stage are included on Figs. 8 and 9.

#### Discussion.

The detailed experimental analysis of gelation here presented seems to indicate two molecular processes, more or less distinct. On the one hand, in its gradual acquirement of viscosity and, moreover, of a viscosity anomalous in the sense that the viscosity varies with the rate of

shear (Figs. 4 and 9), the sol resembles a suspension of which the disperse phase is increasing in size, or occupying a greater proportion of the whole volume. On the other hand, in a gel these aggregates link together throughout the substance, binding the structure in such a way that rigidity is acquired. In the case of agar gel this cohesive force is very strong, and the gel is very difficult to disrupt. The behaviour of the cellulose nitrate sol emphasises the independence of the two processes.

This picture of the molecular changes which are at work is not new, but the point which is brought home by these experiments is the suddenness of the latter transformation and the acquirement of elasticity. This latter factor distinguishes it from a suspension. Indeed, a suspension may be concentrated enough for parts of it to move as a rigid whole under small shearing forces, but, nevertheless, it always yields eventually to a sufficient shearing force. On the other hand, there seems no need to postulate a critical shearing stress, below which flow will not take place, as Pichot\* does; in fact, there is no evidence for this before the gel has set, and after it has set, such critical stress as may be observed is simply that necessary to tear away the fibrils which unite the gel to the solid boundary.

I wish to thank Professor W. E. Curtis for placing every facility of the laboratories at my disposal during this research, and Mr. D. Weatherly, a student, for assistance in obtaining the data relevant to Figs. 2 and 3.

\* J. de Physique, 3, 205, 1932.

# THE INVESTIGATION OF THIN SURFACE FILMS ON METALS BY MEANS OF REFLECTED POLARIZED LIGHT.

By Leif Tronstad (Trondheim, Norway).

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In classifying the properties of a metal, distinction must be drawn between the *internal* and *external* properties. Thus thermal and electrical conductivity, as well as the magnetic and elastic characters, are internal properties, whilst surface tension, the electrolytic, catalytic, photoelectric, thermionic and optical characteristics may be regarded as external. Since, however, the external properties are greatly influenced by the surface condition, and are especially affected by the presence of a non-metallic surface film, it is very difficult to obtain the true relationship between the internal and the external properties of a metal experimentally, unless the influence of the surface conditions be known. In almost all experimental work conducted on apparently clean metal surfaces, one has to deal with a thin *invisible oxide film*, formed in the presence of traces of oxygen. Consequently the investigation of the properties of these thin films and of their influence upon metallic properties possesses the greatest importance in Metallographic Research.

Even from a more general standpoint, the investigation of the thin surface layers on metals deserves attention, since often a detailed knowledge of the film itself is an important matter; for instance, in adsorption, surface migration, friction and in the study of monomolecular films.

Regarding the experimental methods available for the investigation of invisible surface films on metals, it is evident that the examination of nearly all the external properties mentioned above might be of service.1 Apart from methods depending on electron-diffraction and X-rays, however, the optical methods seem at a low temperature-range to be the most suitable for the purpose, especially those based on the examination of polarized light reflected from the metallic surface. Such methods proposed by Jamin and Quincke have been improved by Voigt and Drude,2 who developed the fundamental theory of the subject, besides carrying out the first experiments. Compared with other methods the optical method possesses many advantages. Thus, whilst the electron and X-ray investigations are limited to metals in gases or in vacuo, the measurements of changes in the polarization of light can be performed in any transparent medium, for instance, in solutions. For thin films of about 10-50 Å. average thickness the sensitivity of the method is very good.

Nevertheless, the optical method of Voigt and Drude has until lately been neglected, and a brief survey of the theoretical and experimental side of the method and some of the recent results may not be out of place.

The principle of the method is as follows: 3 A beam of polarized light, when reflected at a metal surface, suffers a change in the state of polarization. The change depends on the angle of incidence and on the optical properties of the metal, being affected by a surface film as well as by the surrounding medium. Consequently, if the angle of incidence is known, as well as the optical properties of the clean metal surface and of the surrounding medium, it is possible from the measurements of the change in the polarization to draw conclusions as to the optical and other properties of any surface film present. By using monochromatic light of different wave-lengths, information regarding the dispersion of the film can also be obtained.

The optical method may also be used on non-absorbing media (glass, water, etc.) covered with surface films,4 but this introduces difficulties owing to the small intensity of the reflected beam.

#### Experimental.

Experimentally, it is necessary to examine the change of polarization of monocrhomatic light, reflected at various angles of incidence from clean and from film-covered metal surfaces. The most convenient course is to measure two quantities: The phase-retardation  $\Delta$ , and the ratio of the absorption coefficients  $\tan \psi$ . The electric vector of the incident light is resolved into two components  $I_{v}$  and  $I_{v}$  which are respectively parallel and perpendicular to the plane of incidence. From the optics of the metallic state, it is known that the two components  $I_v$  and  $I_v$  are retarded in phase and reduced in amplitude to different extents by the reflexion.

<sup>&</sup>lt;sup>1</sup> As shown by Langmuir and his collaborators (compare, for instance, J. Am. Chem. Soc., 53, 486, 1931), electron emission provides an important means of studying the properties and detecting the presence of surface films on metals at higher temperatures. Also measurements of the accommodation coefficient may be employed (*Physic. Rev.*, 40, 78, 1932).

2 P. Drude, *Wied. Ann.*, 53, 481, 1890, and previous papers.

<sup>&</sup>lt;sup>3</sup> A detailed description of the experimental as well as the theoretical side of the method is given by L. Tronstad, Det Kongelige Norske Videnskabers Selskabs Shrifter, Nr. 1, pp. 1-248, 1931. This paper, hereafter referred to as I, contains a detailed bibliography.

<sup>4</sup> Compare, for instance, the textbook of Drude, "Theory of Optics," or Ch. Bouhet, Ânn. de Physique (10), 15, 5, 1931.

If  $\delta_v$  and  $\delta_p$  represent the retardation of  $I_v$  and  $I_p$  respectively, and  $R_v$  and  $R_v$  the amplitudes of the electric vectors after reflexion,  $\Delta$  and  $\psi$  are given by the following equations:

$$\Delta = \delta_p - \delta_v,$$
  $\tan \psi = rac{I_v}{R_v} / rac{I_p}{R_p}.$ 

A diagram of the optical system is shown in Fig. 1. An instrument designed for the examination of horizontal surfaces such as mercury or water, as well as for vertical surfaces, was constructed for the present author by Dr. C. Leiss of Berlin-Steglitz. Instead of a monochromator, a mercury-cadmium light with filters is employed, and, instead of a slit, diaphragms of various diameters. The central table of

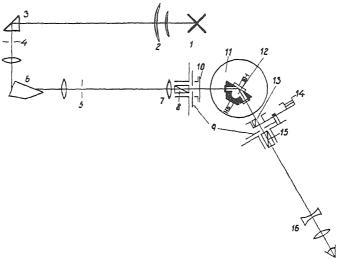


Fig. 1.—The optical system. 1. Light source. 2. Condenser. 3. Total reflecting prism. 4 and 5 Monochromator slits. 6. Lenses and constant-deviation prism of the monochromator. 7. Collimator lens. 8. Polarizer and its scale. 9. Diaphragms. 10. ½-wave plate of mica (Sénarmont compensator). 11. Central table. 12. Metal mirror (treated as anode or cathode in an electrolytic cell). 13 and 14. Half-shade systems. 15. Analyser and its scale. 16. Telescope.

the new instrument is a separate piece, in order that any disturbances produced during the adjustment of the scales shall not affect the surface of the liquid under observation.

The method of measurement is as follows: By turning the polarizer, a parallel beam of light receives linear polarization at a known azimuth in relation to the plane of incidence. By turning the compensator (a quarter-wave mica plate), the two vector components  $I_v$  and  $I_p$  receive a phase-difference just sufficient to compensate for the phase-difference produced by the reflection. The positions of the polarizer and the mica in exact compensation are obtained by matching on the ellipticity half-shade system. In this case  $\Delta$  can be computed from the vibration-directions of the polarizer and the mica referred to the plane of incidence as zero, which readings are read from divided circles.

The reflected light is plane polarized, and should, on the assumption that both components are absorbed (or reduced in intensity) to the same extent, have an azimuth  $\theta_2$  (referred to the plane of incidence as zero), which can be calculated from the vibration direction of the polarizer and compensator. Owing to the fact, however, that the absorption-coefficients of the two components are different, the azimuth found with a "Lippich" half-nicol, is different from  $\theta_2$ . It is easy to show that the ratio of the absorption coefficients for the two vectors,  $\tan \psi$ , can be obtained from the calculated azimuth  $\theta_2$  and the measured azimuth a by means of the equation:

$$\tan \psi = \frac{\tan \theta_2}{\tan \alpha}.$$

According to the electromagnetic theory of light, the quantities  $\Delta$  and  $\psi$  are governed by the optical constants of the metal (n, the refractive index and  $\kappa$ , the absorption index). To a first approximation, the equations are as follows:

$$n = \frac{\sin \phi \tan \phi \cos 2\psi}{1 + \cos \Delta \sin 2\psi},$$
  

$$\kappa = \sin \Delta \tan 2\psi,$$

where  $\phi$  is the angle of incidence. The measurement of the quantities  $\Delta$  and  $\psi$  in the manner mentioned above, constitutes an important method of determining the optical constants of metals.

#### Theoretical.

As shown, the optical properties of a metal can be examined by measuring the polarized monochromatic light of various wave-lengths reflected at different angles of incidence. The next step is to develop the connection between the change in the reflected polarized light (i.e., in the quantities  $\Delta$  and  $\psi$ ), caused by the formation of a non-absorbing surface film, and the optical properties of that film.

The  $\Delta$ - and  $\psi$ -values obtained on a film-free metal and on same metal coated with a non-absorbing film will be written as  $\overline{\Delta}$ ,  $\overline{\psi}$ , and  $\Delta$ ,  $\psi$ , respectively. Supposing the film to be a homogeneous isotropic dielectric layer, the existing equations, to a first approximation, may be written:  $^5$ 

$$\begin{split} \Delta - \bar{\Delta} &= -\frac{4\pi L}{\lambda} \, \frac{\cos\phi \, \sin^2\phi}{(\cos^2\phi - n_0{}^2a)^2 + n_0{}^4a'^2} (n_1{}^2 - n_0{}^2) \\ & \left[ (\cos^2\phi - n_0{}^2a) \Big(\frac{\mathrm{I}}{n_1{}^2} - a \Big) + n_0{}^2a'^2 \Big], \\ 2\psi - 2\bar{\psi} &= \sin 2\bar{\psi} \cdot \frac{4\pi L}{\lambda} \, \frac{\cos\phi \, \sin^2\phi}{(\cos^2\phi - n_0{}^2a)^2 + n_0{}^4a'^2} (n_1{}^2 - n_0{}^2) \\ & \left[ n_1{}^2a' \Big(\frac{\mathrm{I}}{n_1{}^2} - a \Big) - (\cos^2\phi - n_0{}^2a)a' \right], \end{split}$$
 where 
$$a = \frac{\mathrm{I} - \kappa^2}{n^2(\mathrm{I} + \kappa^2)^2}, \quad \mathrm{and} \quad a' = \frac{2\kappa}{n^2(\mathrm{I} + \kappa^2)^2}. \end{split}$$

<sup>5</sup> P. Drude, loc. cit.; L. Tronstad, I, loc. cit. and Z. physikal. Chem., A158, 387, 1932. (This latter paper is hereafter referred to as II.)

Here  $\lambda$  represents the wave-length,  $\phi$  the angle of incidence, n and  $\kappa$  the optical constants of the clean metal, and  $n_0$  the refractive index of the surrounding medium. L is the average film-thickness and  $n_1$  the average refractive index of the non-absorbing film. In these equations all the quantities except L and  $n_1$  are either known or can be measured, thus rendering possible an approximate calculation of the two unknown quantities L and  $n_1$ .

In this respect, it may also be mentioned, that C. Strachan, working with Professor Fowler in Cambridge, has deduced equations similar to those of Drude, starting from different assumptions. Using a method developed by C. G. Darwin, the layer was treated as a volume distribution of Hertzian oscillators. Thus, the equations already published by Drude, based upon simple assumptions, must be considered as sufficiently accurate for the present purpose, especially as the errors caused by lack of homogeneity in the thickness and the optical properties of the film are the predominant ones. Drude has also provided some experimental evidence for his equations.<sup>2</sup> Attention should, however, be called to the fact that films whose optical properties lie close to those of the underlying metal or the surrounding medium, are unsuitable for optical examination.

# Applications of the Optical Method.

## (a) The Passivity of Metals.

The field in which the optical method has hitherto been most fruitful is the Passivity of Metals. As is well known, passivity is met with, when certain metals are immersed in oxidising solutions or receive anodic treatment at high current densities.7

In assessing the value of the optical results obtained, it must be remembered that a century ago Faraday published an explanation of the phenomenon, suggesting that the effect was caused by a surface film of oxygen or oxide, which protected the underlying metal against attack ("mechanical passivity"). Hittorf denied this explanation and attributed passivity to a change within the metal itself ("chemical passivity"). A division between the two rival theories of passivity should be possible by suitable optical methods: if Faraday were right, the metal ought to show a smaller power of reflexion in the passive than in the active state. This question was examined by Königsberger and Müller,8 but they found no appreciable difference, although the method used, in their own opinion, should have been capable of detecting the presence of monomolecular oxygen film. This result has been quoted in the text-books as important evidence against the theory of Faraday.

Nevertheless, recent work on passivity and corrosion seems to show that passive metals are really covered with an oxide film. It therefore becomes important to obtain optical evidence of the presence of that film, and here, owing to its sensitivity, the method of Drude would seem to be the most suitable.

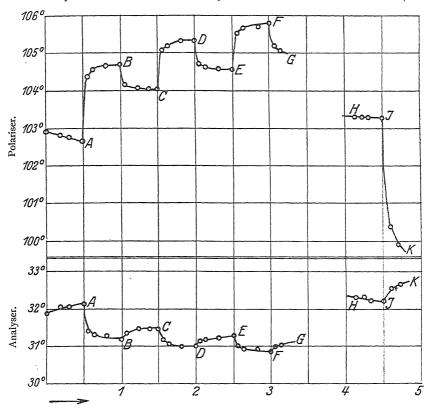
By such methods some evidence of the existence of a surface film on iron and chromium, rendered passive in nitric acid, was obtained several

 <sup>&</sup>lt;sup>6</sup> C. Strachan, Proc. Camb. Phil. Soc., 29, No. 1, 1933.
 <sup>7</sup> Compare the useful survey on the subject by U. R. Evans, Nature, 128,

<sup>&</sup>lt;sup>8</sup> J. Königsberger and W. J. Müller, *Physikal. Z.*, 12, 606, 1911, and previous papers.

years ago by Micheli 9 and later by Bernouilli. 10 In this work, however. the metal mirrors were taken out of the solution and measured in air, thus an oxidation of the surface might have occurred after the metal had been rendered passive, and the optical change detected might equally well have been due to this oxidation.

In the recent optical investigations on the subject, which were performed by the author in the laboratory of Professor Freundlich in Berlin, 11



Time in hours.

Fig. 2.—Iron in 0.5 N. NaOH, I N. Na<sub>2</sub>SO<sub>4</sub>. Current density under stationary conditions: 0·2-0·4 ma/cm². From zero to A: Cathode. A-B: Anode. B-C: Cathode. C-D: Anode. D-E: Cathode. E-F: Anode. F-G: Cathode. H-J: Treatment in N.  $H_2SO_4$ . J-K: Anode in the acid solution,  $D_A =$ 15 ma/cm<sup>2</sup>.

the mirrors received anodic and cathodic treatment and were kept in the solution during the optical examination. As will be seen from the graphs, quite large changes in the optical properties occurred during the anodic treatment of iron and nickel in alkaline and acid solutions respectively. Only the positions of the polarizer and the analyser, from

<sup>&</sup>lt;sup>9</sup> F. J. Micheli, Archives des Sciences physiques et naturelles (Geneva), 10, 125-127, 1900.

10 A. L. Bernouilli, *Physikal. Z.*, **5**, 632, 1904.

1 Z. *Physikal. Chem.*, **A142**, 241,

<sup>11</sup> L. Tronstad, Z. physikal. Chem., A142, 241, 1929 (hereafter referred to as III), and Nature, 124, 373, 1929.

which can be derived directly the  $\Delta$ - and  $\psi$ -values, are given in the graphs. The changes observed during the first passivation correspond to the presence of oxide films of 20-40 Å. average thickness in the passive

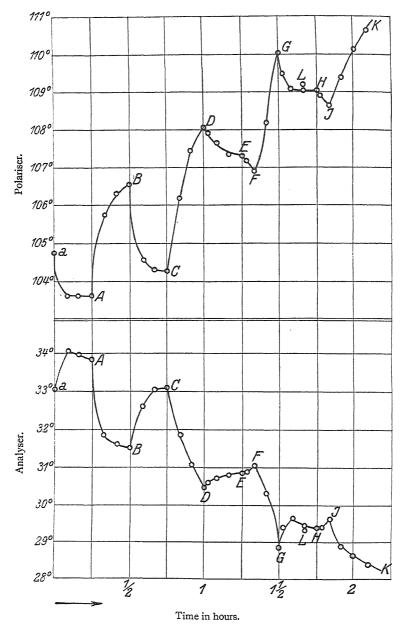


Fig. 3.—Nickel in o·1 N. H<sub>2</sub>SO<sub>4</sub>, o·3 N. Na<sub>2</sub>SO<sub>4</sub>. Current density under stationary conditions: 13-15 ma/cm<sup>2</sup>. a-A: Cathode. A-B: Anode. B-C: Cathode. C-D: Anode. D-E: Cathode. E-G: Anode. G-H: Cathode. H-K: Anode.

state. By rendering the mirror active and passive alternatively, the film was made visible through interference colours.

Thus, the first attempt to detect the surface film present in the state of anodic passivity was successful. The reason why Königsberger and Müller had not been able to detect a film of the dimensions given above, is, probably, that the measurements of the intensity of reflected light are

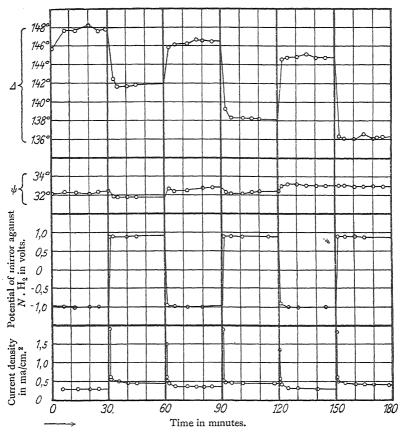


Fig. 4.—Iron 0.04 per cent. C. in 0.5 N. NaOH, N. Na<sub>2</sub>SO<sub>4</sub>. Current density under stationary conditions: 0.3-0.5 ma/cm². 0.30: Cathode. 30-60: Anode. 60-90: Cathode. 90-120: Anode. 120-150 Cathode. 150-180: Anode.

greatly influenced by the smoothness of the metal surface.<sup>18</sup> The author intends to go further into this question on another occasion.

The presence of the film being proved, the next step was to seek quantitative information regarding its properties by the same optical method. This demanded metal mirrors of a very high quality quite free from scratches and from thicker oxide films or other surface films formed

<sup>&</sup>lt;sup>12</sup> The X-ray investigations by F. Krüger and E. Nähring, Ann. Physik, (IV).
84, 939, 1927, failed.
<sup>13</sup> Compare A. L. Bernouilli, loc. cit., and L. Tronstad, I, loc. cit., pp. 27-28.

during polishing. These later investigations were carried out in the laboratory of Professor Benedicks in Stockholm. 14

The different iron and steel specimens (including stainless steel) were ground on lead discs with Wellsworth Emery and then polished with aluminium oxide. Polishing with rouge was found to give dense oxide films. The mirrors were then treated as cathodes and anodes in alkaline, neutral and acid solution at different current densities (18° C.). Some of the results obtained in alkaline solutions are shown in Fig. 4.

Emphasis must be laid on the fact that the  $\Delta$ -values increase by about 2° during the first cathodic treatment. According to Freundlich,

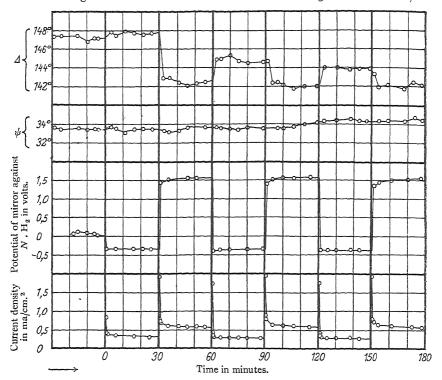


Fig. 5.—Austenitic stainless steel 18 per cent. Cr and 7 per cent. Ni in o 1 N. H<sub>2</sub>SO<sub>4</sub>, N. Na<sub>2</sub>SO<sub>4</sub>. Current density under stationary conditions: 0·3-0·6 ma/cm<sup>2</sup>. Up to 0: Under the action of the acid solution alone. 0-30: Cathode. 30-60: Anode. 60-90 Cathode. 90-120: Anode. 120-150: Cathode. 150-180: Anode.

Patscheke and Zocher, this change corresponds to the removal of an air-formed oxide film. However, it is very likely that the removal is incomplete; the optical difference might equally well be explained by an alteration into a very porous or spongy film. 16. After making the metal passive changes of about  $-6^{\circ}$  in the  $\Delta$ -values and about  $-\frac{1}{2}^{\circ}$  in

<sup>14</sup> L. Tronstad, I and II, loc. cit.; further Nature, 127, 127, 1931.

<sup>15</sup> H. Freundlich, G. Patscheke and H. Zocher, Z. physikal. Chem., 128, 321,

<sup>1927: 130, 289, 1927.

16</sup> L. Tronstad, II, loc. cit., p. 383, compare also L. Tronstad, Det. Kongelige
L. Tronstad, II, loc. cit., p. 383, compare also L. Tronstad, Det. Kongelige
L. Tronstad, Det. Kongelige as IV) and Z. physikal. Chem., 161A, 154, 1932.

the  $\psi$ -values were observed. Several facts indicate a  $\Delta$ -value of about 148° as being the value for clean metal free from any film, and thus. according to the equations quoted, the change corresponds to the presence of a film having an average thickness of about 30 Å. and an average refractive index about 3.0. The refractive index of the iron oxide in bulk was found by Kundt 17 to be 2.6, and consequently, the results must be considered to afford evidence for the oxide theory of passivity. On continued anodic treatment, no appreciable change occurred. Actually, this fact indicates the film to be protective, that is, impenetrable by the ions of the solution. On reactivation, the optical change was partly reversed, thus indicating an alteration in, or a partial removal of, the surface film present in the anodic state. By making the mirror active and passive alternately, the thickness increases gradually, 18 and finally the optical properties came to correspond to an oxide film of about 80-100 Å. average thickness. A surface film of such dimensions should be invisible to the naked eye when examined by vertical light. At grazing incidence, however, first order interference colours should appear, and this was actually confirmed by observation.

The curves obtained by using the different iron specimens in the alkaline, neutral and acid solutions were similar to those shown in Fig. 4. Fig. 5, for example, shows a curve obtained with an austenitic stainless steel in acid solution. But the natural oxide film in this case, being very thin, is stable, and, indeed, rather difficult to remove. However, the change in the optical properties produced during the next passivation again corresponds to a film of about 30 Å thickness and a refractive index of about 3. These values for the film formed during the first passivation could be confirmed with sufficient accuracy in all the experiments carried out.

The curves obtained also lead to other important conclusions regarding the passivity of metals; but reference must be made to the author's previous papers. 19 The results quoted above, may, however, suffice as examples of the application of the optical method to this subject. Much work still remains to be carried out, and the author hopes to be able to record new results in the near future.

# (b) The Oxidation of Metals and Atmospheric Corrosion.

It is well known that iron and several other metals, after being exposed to air, change their behaviour towards reagents which normally attack them. This change was supposed to depend on the formation of a very thin invisible oxide film (the natural oxide film mentioned above) which protects the underlying metal.

In 1927, Freundlich, Patscheke and Zocher succeeded in obtaining evidence of the existence of this film by using the optical method of Drude.<sup>20</sup> They stated that iron mirrors, produced on glass from iron

A. Kundt, Wied. Ann., 34, 484, 1888.
 Compare also U. R. Evans, Nature, 125, 130, 1930.
 L. Tronstad, I, II, III and IV, loc. cit. However, with respect to the importance of the optical method in question, W. J. Müller and collaborators (compare W. J. Müller and W. Machu, Z. physikal. Chem., A161, 150, 1932, seem to main-

tain a standpoint different from that of the present author.

20 H. Freundlich, G. Patscheke and H. Zocher, loc. cit. The natural oxide film on tungsten has also been detected by means of electron diffraction (compare for instance, W. Boas and E. Rupp, Ann. Physik, (V), 7, 983, 1930. See also ibid. (V), 13, 1, 1932). The electro-nemission gave also evidence of the oxide film. (Compare I. Langmuir, loc. cit.)

carbonyl in vacuo, were rapidly dissolved by nitric acid of concentration 1:1. But, after exposure to air, at room temperatures, the mirrors were only very slowly dissolved, leaving brown flakes, which probably represented the natural oxide film. In order to obtain optical evidence of the formation of the natural film, the optical properties of the vacuum mirrors before and after exposure to air were determined. The measurements gave a difference in the  $\Delta$ -values of about 2°, which corresponds to an oxide film of about 10 Å. average thickness, i.e., a film thinner than the film present on iron made passive by the anodic treatment. Evacuation failed to produce the reverse change, which shows that genuine oxidation of the metal had actually taken place, and not merely an adsorption of oxygen.

The method has also been employed successfully by the Dutch investigators.21 A study of the action of air on mercury at room temperature revealed the rapid formation of a film of about 15-20 Å. average thickness, which protected the mercury against further oxidation. However, the accidental double refraction in the windows of the cover (= the so-called "window-effect") seems not to have been taken into account sufficiently and the values quoted may, therefore, be open to

criticism.

In this connection the work of Hauschild 22 deserves mention. Here the change in the optical properties of iron mirrors was followed during the action of moist air, containing carbon dioxide. The changes found indicated the formation of porous surface films. The investigation of Hauschild leads to the problems of atmospheric corrosion, a field in which the optical method might well be adopted. As shown by Vernon 23 and also by Evans,<sup>24</sup> protective films on metals can be obtained by exposure to agents in different ways. The films are usually invisible to the eye, and should, therefore, be suitable for optical examination by the method of Drude.

# (c) Adsorption.

In studying the adsorption of gases on metals, the method might also be valuable. The results mentioned in discussing the oxidation of metals may of course be considered as a "chemi-sorption" of oxygen. In this respect, however, attention should be called to the investigations of Herschkowitsch.25 Exposing clean mercury surfaces to different gases at room temperature, a distinct change in the optical properties could be observed, the  $\Delta$ -values changing by about 1°-2°. When the gases were pumped off, a partial change occurred in the reverse direction a fact which indicates that the process was in part one of adsorption. The gases employed, however, were not properly purified and traces of oxygen must have been present. The irreversible part of the optical change may, therefore, be attributed to the presence of an oxide film.

Although the numerical results of Herschkowitsch are not reliable. the work is very interesting as showing that the optical method can give valuable information regarding an adsorbed phase. When considering

<sup>&</sup>lt;sup>21</sup> Compare, for instance R. Sissingh and J. J. Haak, Proc. Roy. Acad. Sci. <sup>22</sup> Compare, for instance R. Sissingi and J. J. Fraar, 1700. Inoy. Avail. Sci. (Amsterdam), 21, 678, 1919; C. A. Reeser, Physica, 2, 135, 1922, and Arch. Neérland. Sci. (3a), 6, 225, 1923; J. Ellerbroek, Arch. Neérland. Sci. (3a), 10, 42, 1927.

<sup>22</sup> H. Hauschild, Ann. Physik, (IV), 10, 816, 1920.

<sup>23</sup> W. H. J. Vernon, Trans. Far. Soc., 27, 255, 1931, and previous papers.

<sup>24</sup> U. R. Evans, J. Chem. Soc., 1020, 1927; ibid., 92 and 2651, 1929.

<sup>25</sup> E. Herschkowitsch, Ann. Physik, (V), 10, 993, 1931.

adsorption problems, therefore, due attention should be given to optical methods.

# (d) Monomolecular Films on Metals and other Fields of Application.

In the examples mentioned above, nothing was known about the surface films in advance. In order to test the reliability of the method, it is important to apply the method to films with known properties. For this purpose monomolecular films of long-chain fatty acids and alcohols seem to be suitable, since here X-ray examination and measurements of the elastic properties by means of the Langmuir trough have already furnished some information regarding the structure and dimensions of the films.<sup>26</sup> These films must, however, in exact investigations be considered to be optically anisotropic. A theoretical treatment of this case has been given by Strachan,<sup>6</sup> who has discussed the effect of a single layer of molecules on the light reflected from a surface.

Experimental work on this subject has been carried out by C. G. P. Feachem and the author in the laboratory of Professor Rideal at Cambridge, employing the cleanest mercury surface possible in nitrogen free from oxygen. The results are to be published elsewhere in detail. Here it may suffice to mention that the method was not only sensitive enough to detect the optical change produced by the film, but it was also possible to follow the change taking place due to contamination of the mercury surface and irregularities in the surface film. The optical properties of the fatty films, calculated from the measured change in the  $\Delta$ - and  $\psi$ -values by means of the equations given above correspond sufficiently closely with the actual properties of the films. This agreement may be regarded as affording evidence for the approximate correctness of the equation of Drude.

Finally, reference may be made to some other possibilities of the optical method, hitherto completely overlooked.

## (e) Heterogeneous Catalysis.

Though the active centres are considered as the essential constituents of the surface, it is not unlikely that the chemical reaction also takes place to a certain extent outside those centres, provided that contamination is avoided. Besides destroying the active centres, the poisoning of the catalyst may depend on the formation of inactive or protective films on the surface. Knowledge regarding the manner in which the poison acts should make it easier to take effective precautions for preserving the catalyst from deterioration.

## (f) Surface Migration.

The fundamental work of Volmer and his collaborators indicates that surface migration is a very important factor in all problems of surface chemistry.<sup>27</sup> By focusing the eyepiece of the instrument described above *directly upon the surface*, it should be easy to follow the slow movement of a surface phase over a metal mirror (e.g., iodine over copper, oxygen over mercury, etc.).

Several other examples, illustrating the application of the optical method, could be quoted (e.g., lubrication and friction, casting of alloys, 28

 <sup>&</sup>lt;sup>26</sup> Compare for instance, E. K. Rideal, Surface Chemistry, Cambridge, 83, 1930.
 <sup>27</sup> Compare M. Volmer and G. Adhikari, Z. physikal. Chem., 119, 46, 1926.

<sup>&</sup>lt;sup>28</sup> Private communication from P. Bergsöe, Copenhagen.

flotation of ores and minerals, etc.). Those given above may, however, be sufficient to make clear the importance of the method in examining the reactions occurring on metallic surfaces. The method is still in an early stage of development and several improvements in technique as well as advances on the theoretical side may be looked for. But the facts already accumulated definitely established the utility of Drude's method in several branches of Research.

### Summary.

1. A survey is presented of the experimental and theoretical aspects of Drude's optical method, which uses reflected polarized light in the examination of metallic surfaces.

2. As examples are mentioned some of the results hitherto obtained in investigating: (a) The passivity of metals, (b) The oxidation of metals, (c) The adsorption on metals, (d) Monomolecular films on metals.

3. Attention is called to some other fields in which the optical method

may prove fruitful.

The work of the present author carried out for the last four years, has been largely supported by grants from "Nationalgaven til Chr. Michelsen" and from "Den Tekniske Höiskoles Fond," and the author would take this opportunity to express his sincere thanks. The author is also indebted to Dr. U. R. Evans for help in correcting the manuscript.

Norges Tekniske Höiskole, Institutt for Uorganisk Kjemi, Nov., 1932.

# THE CAPILLARY DEPRESSIONS OF MERCURY IN CYLINDRICAL TUBES AND SOME ERRORS OF GLASS MANOMETERS.

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To determine pressures accurately by a mercury manometer account must be taken of capillary depressions. Much uncertainty exists as to the magnitude of this correction and possibly for this reason some investigators have entirely neglected it in accurate determinations of pressure. The cause of this uncertainty lies in the difficulty attaching either to the theoretical calculation or the experimental determination of these depressions. The former depends not only on the surface tension of mercury, but also on the volume and angle of contact of the meniscus, the last of which especially is very difficult to obtain. The experimental measurements, on the other hand, may very easily be vitiated by errors due to refraction in the glass, which for ordinary manometer tubes of 15 mm. or so diameter may be almost as great as the depressions themselves.

In practice the height of the mercury meniscus is used as a measure of the capillary depression. The first theoretical calculations of this relationship were made by Schleiermacher, who worked out a short table for tubes of a few sizes, assuming Gay Lussac's value 0.4425 gm.

per cm. for the surface tension of mercury. Later a much fuller table was calculated by Delcros from formulæ deduced by Schleiermacher. assuming for the surface tension of mercury 0.4426 gm. per cm.<sup>2</sup> An extract from this table, giving also some interpolated values, has been given by Süring 3 in a critical survey of capillary depressions. More recently a full theoretical table has been deduced by Gould, assuming for the surface tension of mercury 0.444 gm. per cm.4 A comparison between the tables of Schleiermacher-Delcros and Gould shows that for tubes varying in diameter from 2 mm. to 14 mm., the calculated depressions are identical to 0.01 mm. where they are given to that accuracy. Since these are both worked out from first principles using almost the same surface tension for mercury, this agreement would be expected, provided that a similar form for the meniscus had been assumed in each case. A theoretical deduction of these depressions has also been given by Maltezos.<sup>5</sup> His results, which apply to tubes greater than 4 mm. diameter are of the same order as those of Schleiermacher-Delcros, but indicate that the relationship between meniscus depression and height is linear rather than curved. Tables obtained theoretically must, however, be subject to some uncertainty, as measurements of the shape and volume of the meniscus have shown that this varies with height in a most complicated way, rendering the calculation of the angle of contact very doubtful.6

On the experimental side determinations have been made by Mendeleeff and Gutkowski 7 which have since been more fully interpolated by Kohlrausch.<sup>8</sup> More recently a small experimental table has been published by Heuse.9 The depressions found by Mendeleeff are very much less than those measured by Heuse. Heuse's results, on the other hand, owing to their large assigned experimental error, namely, 10 per cent. of their value, are in fair agreement with the theoretical tables. The curves obtained by plotting his results for height against depression for a given size of tube do not, however, extrapolate even approximately to zero, as might be anticipated theoretically whatever the form of the menisci.

In view of the above considerations, it appeared that a further investigation of these depressions was desirable. We have accordingly undertaken a series of measurements for tubes of various sizes.

# Experimental Method.

Generally speaking, the method we have used consists in measuring the difference of level of mercury in cylindrical tubes of wide and narrow diameters connected by rubber tubing, since the capillary depression

<sup>&</sup>lt;sup>1</sup> Delcros, Bibliotheque universelle des sciences, belles lettres et arts, Vol. 8, p. 3,

<sup>&</sup>lt;sup>2</sup> Bravais and Martins, Nouveaux memoires de l'acadamie royale des sciences et belles lettres de Bruxelles, Vol. 14, p. 31, 1841.

<sup>&</sup>lt;sup>3</sup> Ber. ü. d. Tatig. d. Kgl. Preuss. Meteorol. Inst. Anhang., p. 35, 1916. Landolt and Börnstein, Tabellen, Vol. 1, p. 72, 1923.

<sup>4</sup> Glazebrook, Dic. Applied Physics, Vol. 3, p. 159, 1923.

<sup>&</sup>lt;sup>5</sup> C.R., 118, 583, 1894.

<sup>&</sup>lt;sup>6</sup> Scheele and Heuse, Ann. Physik, S. (4), 33, 291, 1910. Lohnstein, Ann. Physik, S. (4), 33, 296, 1910. Palacios, Physikal. Z., 24, 151, 1923.

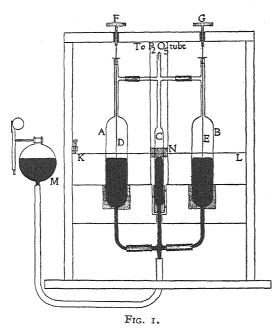
<sup>7</sup> Journ. physik. chem. Ges. Petersburg, 8, 212, 1877; Wied. Beibl., 1, 455

<sup>1877.

8</sup> Lehrbuch. d. prakt. Physik, p. 579, 1901. <sup>9</sup> Z. Instrumentenkunde, 47, 324, 1927.

in a wide tube is negligible compared with that in a narrow. In our experiments the wide tubes had an internal diameter of about 38 mm., and the capillary depression in such tubes is unlikely to exceed 0.001 mm. As our readings were only accurate to 0.005 mm., no error could be introduced in this way. Our narrow tubes ranged in diameter from about 10 mm. to 18 mm.

The general arrangement of the apparatus is shown in Fig. I. A and B are the two wide tubes which were set rigidly in plaster of paris and so arranged that they were exactly parallel to each other. Since the stand carrying them could also be levelled, any refraction errors due to not observing at normal incidence were eliminated. Observations of the mercury surfaces were made with a highly accurate swinging cathetometer carrying a telescope mounted on a micrometer, the error of which did not exceed 0.005 mm. over any part of its range. The tele-



scope was fitted with a sensitive level, and the cathetometer was adjusted so that the telescope could be swung through a complete revolution without change of level. The eyepiece fitted with fine split cross wires. cross wire cannot be set accurately to a mercury surface in large tubes, two needle points D and E were used in the tubes A and B. These could be set to the mercury surface by means of fine micrometer screws F and G. The narrow tube C in which the depressions were being investigated was fixed into

a brass jacket which could be levelled and centred by means of screws. The surface of the tube C was, of course, arranged so as to be exactly parallel to those of A and B, as even slight errors in parallelism might introduce a constant error of 0.01 mm. or more. The tubes were illuminated with a linolite lamp covered with translucent paper. Behind and close to the central tubes was a shutter N carried on vertical wires which could be adjusted to cut off extraneous light from the meniscus. In practice the edge of the shutter must be close to the top of the meniscus, or the true top may not be observed. To ensure dryness the three tubes were connected at the top to a common pentoxide tube which was open to the air. Dryness of the tubes was found to be essential for consistent measurements, the depression being greatly reduced by moisture. The tubes, which were cleaned with hot chromic acid before use, were connected at the bottom to a common reservoir

M, provided with a rack and pinion for adjustment of the meniscus height. The mercury used in all cases had been distilled, filtered and dried. All measurements were made at 21° C. in a thermostatic room.

In carrying out measurements the two needles D and E were set to the mercury surfaces in A and B respectively by observing the mirror images in the telescope, the aperture of which had been reduced to obtain sharpness. The depression was measured by first setting the cross wire to the needle D, then swinging across to the tube C and measuring the difference of level by means of the micrometer screw. This procedure was repeated two or three times with each of the tubes A and B and a mean taken. It will be noticed that by using a tube on each side of C any small error due to lack of level in the swinging would be eliminated. In practice no difference was observed between the two sides, the readings generally agreeing to less than 0.005 mm. The height of the meniscus was then measured, using suitable illumination from the front. Observations were made for menisci of various heights obtained by lowering or raising the reservoir M very slowly. We generally found that it was more difficult to get high menisci than low.

The radii of the various experimental tubes C were found by cutting the tube in two at the average position at which the readings had been taken, and measuring several internal diameters with an accurate travelling micrometer. The tubes were originally selected so that the bore throughout their length was nearly uniform.

## Investigation of Refraction Errors.

Our preliminary measurements showed that a constant error of about 0.01 mm. or more existed between the settings of the points in the tubes A and B, and that this error varied when the tubes were turned in their mounts. Moreover, measurements in a tube C of about 15 mm. diameter and 1.3 mm. thickness of wall gave depressions varying by amounts up to 0.05 mm. in the tube when the meniscus was of the same height, and this error was found in a number of selected tubes. Since the observations on the depression at one point in a tube agreed to 0.005 mm. or less, it appeared likely that a refraction error due to irregularities in the glass was present. To test this a fine horizontal line was arranged behind the tubes and spanning their total width. Since a ruling on glass of suitable length and accuracy was not available, we used a tightly stretched fine horizontal nickel chrome wire KL, fitted with a levelling device. This wire was stretched and levelled, so that when our cathetometer, which had also been accurately levelled, was swung from K to L, no error could be detected along the length of the wire, provided it was not viewed through the glass tubes. On viewing through the glass tubes, however, refraction errors at once became obvious, causing a displacement of the wire up or down even in the centre of the large tubes A and B. With the small tube C these errors were much accentuated, the wire frequently appearing tilted and very irregular. We tested a large number of ordinary tubes in this way, but all showed the error to a greater or less extent. Some of these tubes were kindly examined for us by Mr. W. Taylor of Cooke, Troughton and Simms, who found that these refraction errors appeared to be due to surface irregularities rather than to inhomogeneity in the glass. We then had an optically flat window polished on a cylindrical tube, so

that in the thinnest part the wall thickness was only 0.5 mm., but the refraction due to the plano-concave lens thus formed by the glass made observation impossible. Investigation showed that the task of polishing a thin cylindrical tube both inside and out to a high degree of accuracy was exceedingly difficult. Finally, we found that by using tubes of test-tube thickness, i.e., about 0.3 mm. thickness of wall for the tube C and about 0.6 mm. for the tubes A and B, the refraction error could be entirely eliminated within the limit of accuracy of our measurements  $\pm$  0.005 mm. or less. Since ordinary glass tubes of 15 mm. diameter are about 1.5 mm. thick, a considerable decrease in the error might be expected, but actually the thin tubes appeared to be more accurate than we had anticipated. All our measurements on capillary depressions have accordingly been made with these thin tubes.

We have discussed both the detection and elimination of this refraction error at some length, as hitherto it does not appear to have been studied in detail, and the accuracy of all manometric observations made in ordinary glass tubes must be vitiated by it to a greater or less extent. The error is of the greater importance since it will not in general tend to cancel out.

## Experimental Results.

Experiments were made in tubes of diameters 18·43 mm., 17·39 mm., 17·31 mm., 16·28 mm., 15·46 mm., 14·41 mm., 13·57 mm., 13·41 mm., 11·99 mm., 10·52 mm. When the depressions were plotted against the heights of the menisci, straight lines were obtained in all cases except with the 10·52 mm. tube, in which a slight curvature towards the height axis was detectable. The lines always extrapolated to zero, that is, gave a zero depression for zero height within the limit of error of our experiments. Accordingly, for all the tubes except the last we have obtained a linear relationship between the depression and height by the method of least mean squares, assuming that the line passes through zero. The details of the experiments are given in Table I.

In these tables the first column contains the experimental meniscus heights and the second the experimental depressions. In the third column the depressions are calculated from the least mean square straight lines through the experimental points or in the case of 10.52 mm. diameter tube, are taken from the smoothed curve, whilst the last column gives the difference of the experimental and calculated values. It will

Dep. Calc. Men. Ht. Dep. Exp. Error, Men. Ht. Dep. Exp. Dep. Calc. Error,  $d_e$ , mm.  $d_c$ , mm.  $d_c$ , mm.  $d_e - d_c$ . mm.  $d_o$ , mm.  $d_{o}-d_{o}$ Tube diameter, 18.43 mm. Tube diameter, 17.39 mm. 0.45 0.012 0.014 + 0.001 0.56 0.020 0.023 - 0.003 0.62 0.018 0.020 - 0.002 0.71 0.030 0.030 0.000 0.84 0.022 0.027 - 0.005 1.13 0.047 0.044 -0.0031.09 0.036 0.035 + 0.001 1.22 0.050 0.05T - 0.001 1.33 0.042 0.042 0.000 1.39 0.060 0.058 + 0.002 1.20 0.048 + 0.001 0.047 0.063 1.53 0.063 0.000 1.67 0.054 1·60 0.053 + 0.001 0.066 0.067 - 0.001 1.75 0.075 + 0.002 0.073 Probable error of depressions Probable error of depressions ± 0.002 mm. ± 0.001 mm.

TABLE I.

TABLE I. (cont.)—

	1	·					
Men. Ht. mm.	Dep. Exp. $d_e$ , mm.	Dep. Calc. $d_c$ , mm.	Error, $d_e - d_c$ .	Men. Ht. mm.	Dep. Exp. $d_e$ , mm.	Dep. Calc. $d_c$ , mm.	$d_e - d_c$ .
T	ube diame	ter, 17·31	mm.	$T_{i}$	ube diamei	er, 16·28 1	nn.
0.76	0.031	0.034	0.003	0.39	0.025	0.026	- 0.001
o·89	0.040	0.040	0.000	0.55	0.034	0.038	- 0.004
1.03	0.050	0.046	+ 0.004	0.70	0.048	0.048	0.000
1.16	0.048	0.053	- 0.005	0.82	0.058	0.056	+ 0.002
1.25	0.058	0.057	+ 0.001	1.00	0.070	0.068	+ 0.002
1.32	0.061	0.060	+ 0.001	1.16	0.084	0.079	+ 0.005
1.43	0.066	0.065	+ 0.001	1.32	0.086	0.090	- 0.004
1.55	0.070	0.070	0.000	1.45	0.098	0.099	- 0.001
Pro		or of depre	essions			or of depre	ssions
	士 0.0	002 mm.			± 0·0	002 mm.	
T		ter, 15·38		T	ube diame	ter, 14·41	mm.
0.45	0.039	0.039	0.000	0.54	0.054	0.059	- 0.005
0.20	0.043	0.044	- 0.001	0.64	0.072	0.070	+ 0.002
0.60	0.059	0.053	+ 0.006	0.81	0.085	0.088	- 0.003
0.75	0.070	0.066	+ 0.004	0.90	0.096	0.098	- 0.002
0.85	0.076	0.075	+ 0.001	1.05	0.112	0.112	0.000
0.94	0.088	0.082	+ 0.006	1.22	0.129	0.133	0.004
1.14	0.098	0.100	- 0.002	1.28	0.147	0.140	+0.007
1.27	0.110	0.111	- 0.001	1.39	0.151	0.152	- 0.00I
1.33	0.120	0.117	+ 0.003	1.39	0.154	0.152	+ 0.002
1.42	0.118	0.125	0.007				,
1.50	0.129	0.132	- 0.003				
Pro	bable erro	or of depre	essions	Pro	hable erro	or of depre	esions
		003 mm.		110		002 mm.	3510113
T	ube diame	ter, 13·57	mm.	T	ube diame	ter, 13·41	mm.
0.78	0.095	0.096	- 0.001	0.67	0.084	0.083	1 + 0.001
o·86	0.102	0.106	- 0.001	o∙8i	0.103	0.100	+0.003
1.03	0.130	0.127	+ 0.003	0.96	0.122	0.118	+ 0.004
1.10	0.138	0.136	+ 0.002	1.08	0.142	0.133	+ 0.009
1.24	0.149	0.153	- 0.004	1.25	0.147	0.154	- 0.007
1.35	0.172	0.166	+ 0.006	1.31	0.166	0.162	+ 0.004
1.21	0.186	0.186	0.000	1.41	0.168	0.174	- 0.006
1.65	0.199	0.204	- 0.005	1.52	0.185	0.188	- 0.003
5	"			1.63	0.201	0.301	0.000
Pro	bable erro	or of depre	ssions			or of depre	
		002 mm.				004 mm.	
T	ube diame	ter, 11·99	mm.	T	ube diame	ter, 10·52	mm.
0.46	0.093	0.088	+ 0.005	0.34	0.125	0.118	+ 0.007
0.65	0.124	0.124	0.000	0.44	0.142	0.121	- 0.000
0.74	0.139	0.142	- 0.003	0.53	0.187	0.180	+ 0.007
0.82	0.153	0.157	- 0.004	0.63	0.510	0.210	0.000
0.98	0.192	0.188	+ 0.004	0.70	0.510	0.231	+ 0.008
1.07	0.206	0.205	+ 0.001	0.79	0.263	0.257	+ 0.006
1.12	0.222	0.214	+ 0.008	0.88	0.283	0.280	+ 0.003
1.22	0.230	0.233	- 0.003	1.02	0.314	0.318	- 0.004
1.33	0.246	0.254	- 0.008	1.00	0.314	0.336	0.000
1.37	0.265	0.262	+ 0.003	1.10	0.359	0.363	- 0.004
- 3/	203	0 202	, 5003	1.19	0.388	0.387	+ 0.001
				1.29		0.307	- 0.001
т.	1 11-1				0.415		
Pro		or of depre	essions	Pro		r of depre	ssions
	Ŧ 0.0	003 mm.			± 0.0	004 mm.	
				I			

be seen that the accuracy of measurement is satisfactory, as the probable error never exceeds  $\pm$  0.004 mm. and is in general less.

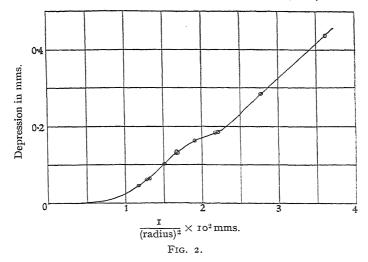
The range diameters of tubes we have studied was the largest over which we found it practicable to obtain satisfactory measurements. With larger tubes the depressions are so small and the difficulties of illuminating the true top of a wide meniscus are so great, that we found it impracticable to continue the series above 19 mm. We also made experiments in tubes of 8.5 mm. diameter, but were unable to obtain concordant results for a constant meniscus height, the error being a few hundredths of a millimetre. This error was not due to refraction, but may have been partly due to slight irregularities in the bore of the tube. It must be remembered, however, that changes in the surface tension of mercury, due to electrification or traces of impurity on the surface, would have a greater effect in narrower tubes. We carefully checked the other tubes for errors of this description but could find no traces of them.

The heights of the menisci measured fall as a rule between about 0.50 mm. and 1.50 mm. As in all cases, except for the 10.52 mm. diameter tube, the relationship between depression and height is linear and passes through zero, it appears likely that extrapolation between meniscus heights of 0 mm. to 1.8 mm. is justified. In the case of the tube of 10.52 mm. diameter, however, the extrapolation is more doubtful, as the line is slightly curved.

## Interpolated Results.

The tables we have already given merely show the depressions corresponding to certain sizes of tubes. To obtain a table for a definite range of size, the results must be interpolated in some way. Now a study of the simple theory of capillary depression indicates that if the depression for a constant meniscus height is plotted against the inverse square of the radii for tubes of different sizes, the relationship should be approximately linear. Actually the theoretically calculated depressions of Gould and others give slight curvatures. Our experimental results when plotted in this way gave a smooth curve of the shape shown in Fig. 2, which is plotted for a meniscus height of 1.5 mm. It will be seen that the curve shows two points of inflection, one corresponding to a diameter of about 14 mm. and the other to a diameter of about 17 mm. This irregularity appeared so unlikely that the depressions over this range were very carefully checked, both by repetition with different tubes of the same or similar diameter and by the investigation of tubes of intermediate sizes. In view of this detailed study we are satisfied that this irregularity is real and have accordingly drawn the curve through the experimental points. It may be pointed out that if a mean curve, disregarding the inflections, were drawn through all the points, the maximum difference in the depressions is only a little over 0.01 mm. Since, however, the greatest divergence of our individual readings from the mean line was never as large as this, whilst the mean lines themselves from which the points were taken had a much smaller error, we obviously could not attribute such deviation to experimental error.

Owing to the difficulty of drawing accurate curves through the points we finally decided to interpolate by two methods. In the first place, we plotted the depressions given by the least mean square lines for meniscus heights increasing by 0·1 mm. from 0·1 to 1·8 mm. and read off the depressions for definite tube sizes. Secondly, we plotted the slopes of the least mean square depression-height lines against the diameters of the tubes and again read off the slopes corresponding to definite sizes. This latter method could, of course, only be used for



tubes from 12 mm. to 19 mm. diameter. These two ways of interpolation gave results agreeing to about 0.002 mm.

A complete table giving the depressions for tubes from 10 mm. to 19 mm. diameter up to a meniscus height of 1.8 mm. is appended. We consider it likely that the figures in this table can be relied on to 0.005 mm., except possibly for the highest menisci in the smaller tubes. A study of the observations indicates that the probable error is well below this limit.

#### Discussion of the Results

The figures given in this table are not in close agreement with other results obtained either theoretically or experimentally. The divergence from the theoretical figures is hardly surprising in view of the difficulty of estimating the correct shape of the meniscus which both Lohnstein and Palacios have shown definitely is not a segment of a sphere. As to the cause of the difference from Heuse's results, we can offer no suggestion, as no details of his experimental method appear to have been published. We have, however, been much struck by the fact that whereas our depression-height curves in all cases tend to give zero depression at zero height, those of Heuse certainly do not do so, even approximately. As there seems to be no doubt that the depression is zero at zero-height, it appears to us highly probable that there is some error in his figures. Actually, our figures agree generally much better with the theoretical tables than with Heuse's results.

In conclusion, we should like to point out the bearing of these experiments on the construction of accurate manometers. In our experience, it is impossible to obtain measurements which can be relied on to 0.01 mm., unless very careful precautions are taken to eliminate

TABLE OF CAPILLARY DEPRESSIONS IN MM.

	8.1	0.565	512	0.454	366	344	165	252	222	200	061	172	.153	0.135	III.	.088	0.075	0.065	0.026	0.049
							0.274 0.		0.500 0					0.127 0						0.040 0
	1.7		_	0.433	_															
	9,1	0.521	0.464	0.411	0.326	0.300	0.258	0.224	61.0	0.181	0.170	0.153	0.136	611.0	260.0	0.078	290.0	0.028	0.020	0.043
	1.5	0.496	0.440	0.380	0.338	0.587	0.242	0.210	0.185	0.170	0.159	0.143	0.127	0.112	0.002	0.074	0.062	0.054	0.046	0.040
	1.4	0.470	0.415	0.366	0.317	0.268	0.556	961.0	0.172	0.159	0.149	0.134	611.0	0.104	980.0	690.0	0.058	0.020	0.043	0.038
	1.3	0.443	0.390	0.343	0.296	0.249	0.210	0.182	091.0	0.145	0.138	0.124	0.110	260.0	6.00	0.064	0.054	0.047	0.040	0.035
	1.3	0.416	0.365	6.316	0.274	0.230	0.194	0.168	0.148	0.136	0.127	0.114	o.ioi	680.0	0.073	0.020	0.020	0.043	0.037	0.033
<u>.</u>	1,1	0.388	0.340	0.295	0.252	0.210	0.178	0.154	0.136	0.125	6.117	0.105	0.003	0.082	290.0	0.054	0.046	0.040	0.034	0.030
ights. mm	0.1	0.359	0.314	0.270	0.230	161.0	191.0	0.140	0.123	0.113	901.0	960.0	0.085	0.075	190.0	0.046		0.036		0.027
Meniscus Heights, mm.	6.0	0.329	0.287	0.245	0.507	0.172	0.145	0.126	O·III	0.102	960.0	0.087	220.0	290.0	0.055	0.044	0.037	0.033	0.028	0.024
Mer	8.0	0.298	0.259	0.220	0.184	0.153	0.129	0.112	660.0	060.0	0.085	0.077	890.0	090.0	0.049	0.039	0.033	0.030	0.025	0.021
	2.0	0.266	0.231	0.194	191.0	0.134	0.113	860.0	0.086	6.00	0.074	290.0	0.059	0.053	0.043	0.034	0.020	0.025	0.022	610.0
:	9.0	0.232	0.201	o.168	0.138	0.115	960.0	0.084	0.074	0.068	0.064	0.057	0.051	0.045	0.037	0.020	0.025	0.022	610.0	910.0
	0.2	0.197	0.170	0.141	0.115	960.0	0.080	0.070	0.062	0.057	0.053	0.048	0.042	0.037	0.031	0.025	0.021	0.018	910.0	0.014
	0.4	0.161	0.138	0.114	0.002	0.077	0.064	0.020	0.040	0.045	0.043	0.038	0.034	0.050	0.025	0.050	0.017	0.014	0.012	0.011
	0.3	0.123	0.104	0.086	690.0	0.057	0.048	0.042	0.037	0.034	0.032	0.020	0.025	0.022	810.0	0.015	0.012	0.011	600.0	800.0
	0.5	0.084	0.000	0.058	0.046	0.038	0.032	0.028	0.025	0.023	0.021	0.010	0.017	0.015	0.012	0.00	800.0	0.00	900.0	0.005
	1,0	0.043	0.035	0.020	0.033	0.010	0.016	0.014	0.012	0.011	0.011	0.010	800.0	0.007	900.0	0.005	0.004	0.004	0.003	0.003
Tube Diameter.	mm.	10.0	10.5	0.11	11.5	12.0	12.5	13.0	13.5	14.0	14.5	15.0	15.5	0.91	16.5	0.71	17.5	18.0	18.5	0.61

errors due to refraction. These errors may be divided into two types, namely those due to irregularities in the walls and those due to observation not being at normal incidence. The latter can be eliminated if the tubes are parallel. The former error is, however, by far the most important, as we have found by direct measurement that errors as great as  $\pm$  0.05 mm. may be obtained with a tube of about I mm. thickness of wall when observed normally. Obviously, by using tubes with walls as thin as possible both types of error are reduced, and we consider that with tubes of 0.4 mm. thickness of wall, manometric measurements are trustworthy to 0.01 mm., provided the limbs are parallel. Actually we have now constructed a manometer of this type, and find that it is entirely satisfactory.

## Summary.

Measurements have been made of the capillary depressions of mercury in cylindrical glass tubes of various sizes. In order to eliminate refraction errors in the glass, it was found necessary to use very thin walled glass tubes. With such tubes it was possible to obtain measurements agreeing to less than oon mm. The results have been interpolated and a detailed table giving the relationship between capillary depression and meniscus height has been deduced for tubes varying in diameter from 10 mm. to 19 mm. and for meniscus heights from 0 mm. to 1.8 mm.

The results are compared with the figures given in other tables and the deviations discussed.

The refraction errors in cylindrical glass tubes have been investigated in some detail and the bearing of these errors on the design of glass manometers considered.

We have much pleasure in thanking the Department of Scientific and Industrial Research and also Imperial Chemical Industries for their financial support. We also wish to record our indebtedness to Professor Whytlaw-Gray for putting every possible facility at our disposal for carrying out this work, and for his interest and criticism.

Leeds University.

## DISSOLUTION OF MAGNESIUM AND MAGNESIUM-BASE ALLOYS BY NATURAL AND ARTIFICIAL SEAWATERS.

By L. WHITBY.

Received 10th January, 1933.

Increased industrial application of magnesium and magnesium-base alloys necessitates extensive corrosion tests, some of which must employ seawater. The difficulties sometimes involved in obtaining adequate supplies of natural seawater have inspired the present investigation which aimed first at recording the difference in the rate of attack of magnesium and some magnesium-base alloys by seawater and by sodium chloride solution, and then at synthesising a solution capable of duplicating the results yielded by the use of natural seawater.

No similar experiments are described in the literature, but Bengough and Lee 1 have recently described corrosion experiments with mild steel immersed in seawater and in certain salt solutions.

## Experimental.

Magnesium.—Magnesium used consisted of foil of commercial grade (99.97 per cent. Mg) and of redistilled grade (99.98 per cent. Mg) 0.2 mm. and 0.4 mm. in thickness respectively; specimens 1.5 by 4.0 cms. were used. Rate of dissolution of the metal was calculated from the amount of hydrogen evolved. Analyses of metal and full experimental details of the corrosion vessel, of the method of measurement and of reproducibility of results, have been published previously.2

Seawater was supplied by the Marine Biological Association and obtained from three miles outside Plymouth harbour, to avoid undue

sewage contamination.

The rates of dissolution were plotted as the mean of two experiments at 25° C., and curves were obtained for the following solutions, 50 c.c. of which were always used:-

I. N/2 sodium chloride.

II. I plus 4.09 g./l. magnesium chloride 6 aq.

III. II plus 3.65 g./l. magnesium sulphate 7 aq.

IV. III plus 1·72 g./l. calcium sulphate 2 aq.
V. IV plus 0·94 g./l. potassium sulphate.
VI. V plus 0·13 g./l. magnesium bromide 6 aq. plus 0·129 g./l. calcium carbonate.
VII. Seawater.

Solution VI contains the salts in the same proportion (starting, however, with N/2 sodium chloride) as they occur in natural seawater; the figures given by Jorissen 3 for the main inorganic constituents of seawater were used.

Magnesium-base Alloys.—Three typical magnesium-base alloys were tested, Elektron AZM, AM503 and VI; compositions are shown in Table I. For comparison one type of duralumin was included in the tests.

Alloy.	Aluminium.	Zinc.	Silicon.	Manganese.	Magnesium.
Elektron AZM (sheet) Elektron AM503	6-15-6-45	0.8-1.2	0-0-2	0.2-0.5	9 <sup>2</sup> •5
(sheet)	-	_	0-0-3	1.3-1.7	98.0
(extruded bar) .	9.2-11.2	0-0-6	0-0-3	0.2-0.2	88·o

TABLE I.—Composition of Alloys Used.

Note.—Compositions are those given by the makers.

AZM alloy was used as 14 S.W.G. sheet 5 cms. square; AM503 alloy was used as 16 S.W.G. sheet 5 cms. square for spray tests and in strips 3 by 7 cms. for immersion tests; VI alloy was used as extruded round bar 2.5 cms. diameter and 6 cms. long; duralumin was used in the form of 16 S.W.G. sheet 5 cms. square.

<sup>&</sup>lt;sup>1</sup> J. Iron and Steel Inst., No. 1, 285, 1932. <sup>2</sup> Trans. Faraday Soc., **28**, 474, 1932; **29**, 415, 1933. <sup>3</sup> Chem. News, III, 67, 1915.

The alloys were tested with natural seawater, 2.5 per cent. sodium chloride solution and artificial seawater (solution V above). Two methods of testing were used, spraying and total immersion. Elektron alloys were cleaned before starting the tests by pickling in 10 per cent. by volume nitric acid; duralumin was cleaned by pickling in 20 per cent. by volume sulphuric acid plus 10 per cent. nitric acid at 95° C.; this bath was found to give a finish free from stains.

Specimens to be sprayed were suspended vertically by gutta-percha covered copper wire on a wooden stand in a field adjoining the laboratory, and were sprayed three times daily by means of a glass atomiser connected to the laboratory supply of compressed air. Totally immersed specimens were suspended from glass hooks in 500 c.c. beakers completely filled with the solutions to be tested; experiments were all performed in quadruplicate.

After completion of the experiments, loss of weight of the metal was obtained by dissolving the corrosion product in a boiling solution of 20 per cent. A.R. chromic acid containing 0.5 per cent. of silver chromate; full details of this method have been published previously, and although used originally for magnesium-base alloys has now been found to be equally effective with duralumin.

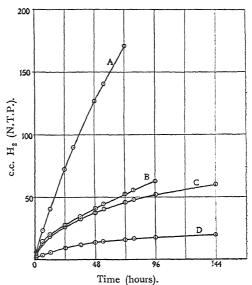
#### Discussion.

**Magnesium.**—Figs. I and Ia show hydrogen evolution/time curves for commercial (MgCI) and redistilled (MgR) magnesium in seawater

and in N/2 sodium chloride solution. In both cases the use of seawater results in considerable diminution in rate of attack compared with the rate in sodium chloride solution; the diminution becomes more marked with progression of the attack. The differences between the commercial and redistilled magnesium are due to the different of degrees of purity of the metal.

The results gain in interest in the light of the work of Bengough and Lee<sup>1</sup> who show that for mild steel an increase in the rate of hydrogen evolution is caused by seawater, compared with N/2 sodium chloride solution.

In order to determine the cause of the diminu-



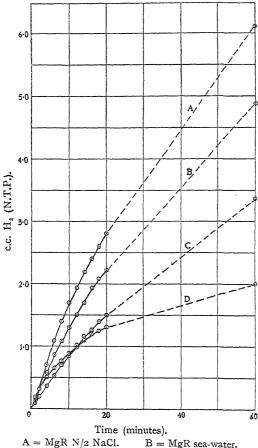
 $\begin{array}{ll} A = MgR \ N/2 \ NaCl. & B = MgR \ sea-water. \\ C = MgC_1 \ N/2 \ NaCl. & D = MgC_1 \ sea-water. \\ Fig. \ r. — Dissolution of magnesium in N/2 sodium \end{array}$ 

Fig. 1.—Dissolution of magnesium in N/2 sodium chloride solution and in sea-water.

tion of attack of magnesium caused by seawater, dissolution experiments

were conducted with MgCI, using the series of solutions already recorded; results are plotted in Figs. 2 and 2a.

Addition of magnesium chloride to sodium chloride cause sa considerable increase in the rate of attack, due probably to the increased chlorine ion concentration. Curve III, Fig. 2, however, obtained from a solution identical with II, except for the addition of a small amount of magnesium sulphate, shows a considerable diminution in the attack. the rate being about one-third of that obtained without the sulphate.



 $C = MgC_1 N/2 NaCl.$  $D = M\breve{g}C_1$  sea-water. Fig. 1a.—Dissolution of magnesium in N/2 sodium chlor-

ide solution and in sea-water. Initial action.

At the same time the appearance of the corrosion product undergoes a marked change, that produced in the liquid by solutions I and II being finely divided and taking appreciable time settle, whereas solution III produces a corrosion product consisting of coarse granular flakes which settle immediately. Solutions I and II produce a corrosion product typical of a metallic hydroxide sol flocculated by a monovalent anion, whereas the product produced by solution III is typical of the same hydroxide flocculated by a divalent anion. It is noteworthy that the latter type of corrosion product appears to be produced bv natural seawater.

The addition of a small amount of calcium sulphate to solution III causes a still further decrease in the rate of attack, as shown by curve IV, and finally solutions V and VI yield

results agreeing very closely with those given by natural seawater.

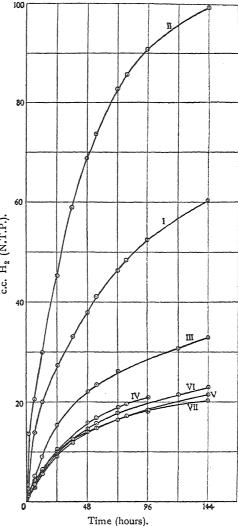
It is clear, therefore, that the differences in question between seawater and sodium chloride solution are due almost entirely to the inorganic constituents present in seawater, sulphates being particularly active in reducing the rate. These results may be contrasted with those of Bengough and Lee for mild steel, the differences there being traced to small amounts of unidentifiable organic matter in the seawater.

It was suggested in a separate communication 2 that the potential

difference between the anodic and cathodic parts of a corroding magnesium surface immersed in a chloride solution was that due to the free

metal (anodes) and the metal ennobled by a film of magnesium hydroxide (cathodes). The further suggestion was advanced that film formation at the cathodes was partly caused by electrophoretic deposition thereon of magnesium hydroxide sol, forming a tightly adherent film capable of ennobling metal. If this mechanism is correct the action of sulphates in presence of chlorides is clear.

A ratio must exist between the rate of floctween the rate of floc- culation of the metallic H hydroxide sol by anions Z present in the solution and its rate of discharge after migration to the cathodes. The actual ratio will depend mainly upon the concentration and valency of the free anions in the solution, the potential difference existing between anodes and cathodes of the metal, the temperature, the charge density and size of the hydroxide micellæ and their distance from the cathodes at the time of formation. addition of the divalent sulphate anion to a chloride solution will result in a much greater rate of flocculation of the hydroxide in the solution so that less sol (if any) is discharged at the cathodes, thus reducing their ennoblement by film formation. The result is that in presence of sulphates the potential differcathodes is less, and there-



ence between nodes and Fig. 2.—Dissolution of magnesium in various salt cathodes is less and there.

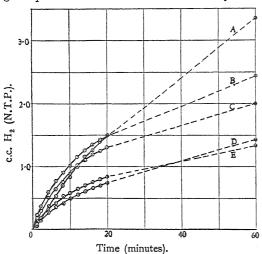
fore the rate of attack is less than in absence of sulphates. Flocculated sol that merely drifts to the metal is unable to form a film coherent

and uniform enough to affect appreciably the interfacial potential of the

part upon which it rests.

The increased hydroxyl ion concentration in both natural and artificial seawater also contributes to the diminution in the rate of attack compared with sodium chloride solution. The mechanism is, however, different from that of sulphate additions and probably affects most the initial parts of the curves, by discharge of an increased number of hydroxyl ions at the primary anodes, resulting in film formation thereon. This is equivalent to irreversible anodic polarisation and is discussed in greater detail elsewhere.<sup>6</sup>

Action of Saponin.—It is known that the foaming properties of seawater are due to traces of compounds which are probably saponins; saponin is present in many varieties of seaweed. The lowering of the gas-liquid interfacial tension caused by such bodies as the saponins



A = I. B = VI + 0.00025 per cent. saponin. C = sea-water. D = III. E = VI.

Fig. 2a.—Dissolution of magnesium in various salt solutions and in sea-water. Initial action.

may have considerable effect reactions on gas films are where present. Möller<sup>5</sup> found that for a series of metals the minimum cathode over-voltage varies with the angle contact between hydrogen bubbles and the metal in dilute sulphuric acid. The angle of contact  $\theta$  is given by

$$\cos \theta = \frac{\sigma_{\rm sg} - \sigma_{\rm lg}}{\sigma_{\rm sl}},$$

where  $\sigma_{sg}$ ,  $\sigma_{lg}$ , and  $\sigma_{sl}$  are the interfacial tensions, electrode-gas, electrolyte-gas and electrode-electrolyte respectively. Consequently an agent

capable of diminishing the electrode-gas and electrolyte-gas tensions should decrease the over-voltage. Thiel and Breuning <sup>6</sup> found that certain substances such as butyric acid and amyl alcohol which decrease surface tension actually raise the over-voltage at a platinum cathode. Such powerfully bathotonic substances, however, will be appreciably adsorbed and thus alter the nature of the electrode-gas-electrolyte interfaces.

The presence of a film of hydrogen on the cathodes of magnesium dissolving in salt solutions is not proved; the action of saponin on the rate of hydrogen evolution should, therefore, be interesting. Figs. 3 and 3a show the results on the rate of hydrogen evolution from MgCI of adding to solution VI 0.00025 per cent. and 0.00125 per cent., respectively, of saponin. A distinct increase in the rate of hydrogen evolution is shown and provides evidence for the presence of obstructive

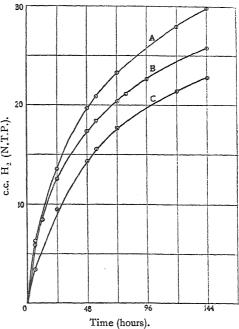
 <sup>&</sup>lt;sup>5</sup> Z. physikal. Chem., 65, 626, 1909; Ann. Physik, 25, 725, 1908.
 <sup>6</sup> Z. anorg. Chem., 83, 329, 1913.

hydrogen films on magnesium dissolving in salt solutions. Bengough and Lee added saponin to some of the solutions that they employed

without noticing any effect on the rate of hydrogen evolution from mild steel. On mild steel, however, hydrogen may form by a reaction which involves no obstructive gas film formation.

In Fig. 2a, it will be observed that, during the initial stages of the reaction, a seawater results in an appreciably greater rate of Z attack than solution VI, although after about one hour good agreement is obtained. It is probable that this is due to the presence of saponins in the sea-water. In Fig. 2a is shown the effect during the intial stages of the reaction, of adding 0.00025 per cent. of saponin to solution VI. The rate is so increased that the curve is now above that given by seawater; there is, however, considerably less than 0.00025 per cent. of saponin in seawater.

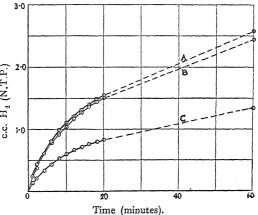
The fact that the difference between seawater and solution VI is great only in the initial stages of the reaction 20 the H is explained by assumption that the z potency of the saponins of seawater is destroyed during the course of the reaction either by reduction with hydrogen or by adsorption on the corrosion product. Confirmation of this view is obtained from the fact that the difference caused by addition of saponin to solution VI is far more marked during



A = VI + 0.00125 per cent. saponin.

B = VI + 0.0025 per cent. saponin. C = VI.

Fig. 3.—Effect of saponin on rate of dissolution of magnesium in artificial sea-water.



 $A = VI + o \cdot 00125 \ per \ cent. \ saponin.$   $B = VI + 00025 \ per \ cent. \ saponin. \ C = VI.$   $Fig. \ 3a. - Effect \ of \ saponin \ on \ rate \ of \ dissolution \ of \ magnesium \ in \ artificial \ sea-water. \ Initial \ action.$ 

the initial stages than during the later stages of the attack; this is shown in Figs. 3 and 3a.

Magnesium-base Alloys.—The losses of weight at the conclusion of the tests of the three magnesium-base alloys tested are shown in Table II; the results in general agree with those obtained for magnesium.

TABLE II.—Corrosion of Magnesium-Base Alloys and Duralumin by Natural and Artificial Seawaters and by Sodium Chloride Solution.

		u .	L	oss of Weight (g.	).	
Alloy.	Type of Test.	Duration (Days).	Seawater.	Art. Seawater.	2.5 Per Cent. Sodium Chloride Solution.	
Elektron AZM.	Intermittent spray.  Total immersion.	28 7	0·82, 0·75, 0·65, 0·78. Mean 0·75. 0·37, 0·69. 0·28, 0·34.	0.96, 1.27, 1.12, 1.14. Mean 1.12. 0.47, 0.46, 0.31, 0.50.	0.75, 1.28, 0.80, 0.76. Mean 0.90. 2.01, 2.65, 2.60, 2.71.	
Elektron AM503.	Intermittent spray. Total immersion	9	Mean 0·42.  1·11, 0·88, 0·77, 0·75. Mean 0·88. 1·51, 2·33, 1·82, 1·39.	Mean 0·43.  0·49, 0·37, 0·33, 0·33, Mean 0·38. 1·36, 1·25, 1·17, 1·84.	Mean 2·49.  2·10, 1·50, 1·20, 1·16.  Mean 1·49. 1·86, 2·78, 1·92, 2·07.	
Elektron VI.	Intermittent spray.	28	Mean 1.76.  0.56, 0.35, 0.47, 0.50. Mean 0.47. 0.34, 0.33,	Mean 1·40.  0·58, 1·11,  0·72, 0·97.  Mean 0·84.  0·56, 0·27,	Mean 2·16.  0·84, 0·63, 0·74, 0·90.  Mean 0·78. 4·53, 4·64,	
Duralumin.	Intermittent spray.	28	0.33, 0.35. Mean 0.34. 0.03, 0.03, 0.02, 0.02. Mean 0.025. 0.02, 0.02,	0.57, 0.29. Mean 0.42. 0.02, 0.02, 0.02, 0.02. Mean 0.02. 0.01, 0.01,	4·58 (11·81) Mean (3) 4·58. 0·04, 0·04, 0·04, 0·04. Mean 0·04. 0·04, 0·04,	
	immersion.		0.02, 0.01. Mean 0.017.	0.02, 0.01. Mean 0.012.	0.04, 0.04. Mean 0.04.	

The spray tests, however, show less difference between natural seawater and sodium chloride solution than that shown by the total immersion tests. The natural obstacles imposed to formation of protective, or other, films during the intermittent drying and wetting of the metal surface, together with the mechanical effect on the films (if any) from the spray itself, no doubt explains the lack of the large differences caused by total immersion. Nevertheless, the loss of weight produced by seawater was always less than that caused by sodium chloride solution. The artificial seawater behaved anomalously in the spray tests, resulting, in the case of AM503 alloy, in a smaller loss of weight, and, in the case of the other two Elektron alloys, in a larger loss of weight, than that produced by natural seawater.

The type of attack resulting from the spray tests was the same with each solution, a general pitting of the surface of the specimen, the interstices between the pits remaining quite unattacked. The large losses of weight of the AM503 alloy (an alloy generally considered to be less corrodible than other magnesium-base alloys) were caused probably by local segregation of a manganese-rich phase, a fault which has been noticed so often with this particular alloy that its relatively non-

corrodible properties when in a homogeneous condition are rarely capable of being observed.

Total immersion tests increase considerably the differences between natural seawater and sodium chloride solution, agreeing excellently with the results yielded by magnesium; moreover, the artificial seawater reproduces closely both the total corrosion and the type of corrosion produced by natural seawater. In general both the artificial and natural seawaters produce isolated pits on the surface of the specimens with the larger part of the surface unattacked but covered with corrosion product. Sodium chloride solution, however, results in far more of the surface being attacked, with the resulting pits not only more numerous but deeper.

Duralumin.—In general, the particular sample of duralumin behaved the same as the magnesium-base alloys; the attack, however, was considerably less, and concentrated in the form of pin-hole pits mainly at the corners and edges of the specimens. Seawater again caused less corrosion than sodium chloride solution both in spray and in total immersion tests; moreover, in both cases the artificial seawater gave excellent agreement with the natural seawater. In the case of the totally immersed specimens, the type of attack was different in sodium chloride solution from that in both natural and artificial seawaters. The corrosion product was concentrated in flocculent tufts around the small pits, the rest of the surface remaining free from all visible penetrative action. Whereas, however, the unattacked surface of the metal after immersion in both artificial and natural seawater was covered only with a thin, loose, almost invisible film, in the case of sodium chloride solution the unattacked surface exhibited a dark bluish-grey interference colour.

#### Summary.

Hydrogen evolution/time curves have been obtained for magnesium in N/2 sodium chloride solution and in seawater. The rate of attack in seawater was considerably less than in N/2 sodium chloride solution; the difference was found to be due almost entirely to the presence of sulphates

An artificial seawater has been prepared capable of reproducing the

hydrogen evolution/time curves given by natural seawater.

The effect of addition of traces of saponin has been investigated and found to increase the rate of hydrogen evolution compared with that resulting from the same salt solution without saponin. This effect is taken to indicate the presence of obstructive hydrogen films on the magnesium.

The losses of weight of three magnesium-base alloys and of one type of duralumin have been obtained after both intermittent spray tests and total immersion tests in natural and artificial sea-water and in 2.5 per cent. sodium chloride solution. The results were substantially the same as those given by pure magnesium, but the differences were not nearly so pronounced after spraying as after total immersion in the different solutions.

The work has been carried out for the Corrosion Research Committee of the Department of Scientific and Industrial Research under the supervision of Dr. G. D. Bengough, to whom the author is indebted for advice and interest. Thanks are due to the chairman, Professor Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, F.R.S., Director of Chemical Research, for permission to publish.

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## INTERFACE CATALYSIS IN THE REDUCTION OF METALLIC OXIDES.

By A. R. UBBELOHDE.

## Received 11th Fanuary, 1933.

Numerous reactions have been reported where the formation of one solid phase from another is catalysed by the presence of the substance to be formed. In the reaction  $CaCO_3 = CaO + CO_2$ , for example, it was first emphasised by Langmuir 1 that the lime must be formed as a distinct phase at equilibrium, since a definite dissociation pressure is set up at constant temperature. Studies of reaction velocity have shown, however, that a system may pass through a number of intermediate states before reaching equilibrium, so that Langmuir's argument is incomplete.

Experiment shows that calcspar decomposes much more readily when some lime is already present. Considerations of the heat quantities involved may ultimately show that the formation of any intermediate state, such as a monomolecular layer of CaO on CaCO3, is highly improbable; this would explain the phenomena observed. An alternative explanation would be that the passage of the CO<sub>2</sub> molecule from the solid to the gaseous state is greatly facilitated by the steep fields of force at the join of two phases (cf. the influence of dust on mist formation, and the superheating of liquids). Until more data are available we cannot decide between the two explanations of this particular case of interface catalysis.

More definite information is available about the reduction of certain metallic oxides, where the reaction is accelerated by the metal formed. This has been variously ascribed to the fact that the reduced metal is only formed as a distinct phase,<sup>2</sup> or that the reducing gas is strongly adsorbed on the metal only, making a large concentration available for reduction at the interface between metal and oxide.3

The object of the present communication is to show that in most cases the high energy required for the formation of any intermediate state leads to reaction almost exclusively at the interface between metal and oxide. A few reactions are found, however, in which intermediate states might be formed without too much difficulty, and for which special mechanisms may be invoked if any interface catalysis is

Consider the reactions (heat evolved positive)

CuO (cryst) + 
$$H_2$$
 = Cu (cryst) +  $H_2$ O + 29 Cals. (1)  
NiO (cryst) +  $H_2$  = Ni (cryst) +  $H_2$ O + 8.8 Cals. (2)

Using the approximate formula for equilibrium due to Nernst.

$$\log (H_2)/(H_2O) = -Q/4.57T - 2.0$$

<sup>&</sup>lt;sup>1</sup> J.A.C.S., 38, 2221, 1916. <sup>2</sup> E.g., A. Benton and P. Emmet, J.A.C.S., 46, 2728, 1924. <sup>3</sup> E.g., I. Langmuir, Trans. Faraday Soc., 17, 620, 1922. Cf. Taylor, Treatise of Physical Chemistry, 2, 1931.

it is clear that in the neighbourhood of 600° K, where the reactions proceed at measurable speed, the right hand side of the equation will be positive only if the heat of reaction is smaller (algebraically) than — 5 Cals. Reactions (1) and (2) thus proceed to completion without

any difficulty.

If the reduction does not take place at an interface, the freshly reduced metal atoms do not necessarily form solid Cu and Ni, with their characteristic lattices, and we are not justified in writing the right hand side of the equations as above. For example, the heat of reaction where only isolated copper atoms are reduced on the surface of copper oxide may be estimated as follows:—

The reaction

CuO (cryst) + 
$$H_2$$
 = (Cu on CuO) +  $H_2$ O +  $Q_1$  . (3)

may be considered as the sum of reaction (1) and the reaction

$$Cu (cryst) = (Cu on CuO) + q_1 . . . . (4)$$

If the heat of adsorption of isolated Cu atoms on CuO were negligible compared with other the quantities involved,  $q_{\mathbf{1}}$  would be the same as the heat change in the process

Since this heat of adsorption will in general not be negligible, the sum of (I) and (5) gives an upper limit to  $\mathcal{Q}_1$  in (3). A lower limit may be estimated from a consideration of the work done when a single O atom is removed from a CuO lattice, leaving one unpaired Cu atom on the surface, i.e. (Cu on CuO). Until more precise data are available, we may assume that the work of removing this unpaired Cu atom against the attraction of the rest of the lattice is only one-ninth of that required to remove the original O atom against the attractions of the rest of the lattice + the attraction of the Cu atom.

Thus since

$$CuO(cryst) = Cu(gas) + O(gas) - 178 Cals.,$$

on the above assumption

CuO (cryst) = (Cu on CuO) + O (gas) - 160·2 Cals.  
and Cu (gas) = (Cu on CuO) + 
$$17\cdot8$$
 Cals. . . . (6)  
Thus Cu (cryst) = (Cu on CuO) +  $q_2$  +  $17\cdot8$  Cals. . . (6a)

Since the heat change in (6) is almost certainly too large, the sum of

(I) and (6a) gives a lower limit to  $Q_1$  in (3).

In the following table,  $H_2 + \frac{1}{2}O_2 = H_2O$  (gas) + 67.7 Cals., and the heats of the reaction  $MO + H_2 = M + H_2O$  given under column I are based on Landolt Börnstein, Tabellen, 6th edition. Under column II are given the heats of vaporisation of the metals; for the sake of uniformity, these are all based on Trouton's formula. The latent heats derived from vapour pressure curves based on effusion experiments are more accurate, and usually somewhat higher, but those based on evaporation from wires may include large "activation energies." Latent heats for Pd and Pt are based on evaporation from wires, in the absence of more reliable data. Columns III and IV give the limits between which the heat change  $Q_1$  in (3) probably lies.

 $<sup>^4</sup>$  Q/Tb = 22·2. Cf. P. Harteck, Z. physik. Chem., 134, 17, 1928.  $^5$  Cf. K. Fajans, Z. Electrochem., 31, 69, 1925, and P. Harteck, loc. cit.

	Ме	tal.	I.	II.	III.	IV.	Kilogram Calories.
Cu Ni Pb Hg Ag Pt (e: Pd (e		(OH) <sub>2</sub> (OH)	29·0 8·8 16·4 46·2 61·2 48·5 45·9	- 58·5 - 75·4 - 41·8 - 14·0 - 49·5 - 127·0 - 101·0	- 29·5 - 66·6 - 25·4 + 32·2 + 11·7 - 78·5 - 65·1	- 11·7 - 45·1 - 8·0 + 43·8 + 25·4 - 55·8 - 44·7	

From the above figures, interface catalysis may be expected in the reduction of the oxides of Cu, Ni, Pt, Pd, Pb. Experiment confirms this for nickel<sup>2</sup> and copper.<sup>6</sup> A similar phenomenon has been observed for platinum oxide.7 In these reactions, water vapour hinders the initial reduction, and oxygen slows down the process at all stages. Fresh metal nuclei are probably formed via an intermediate stage, whose probability of formation has been shown to be very small. The probability that such a stage gets reoxidised by O2 or H2O before it can form a nucleus is conversely very great. Once a nucleus has been formed, however, it grows smoothly till the whole grain of oxide is converted to metal.

No experimental data are yet available for Pd and Pb. The reductions of HgO and Ag<sub>2</sub>O by hydrogen have likewise not been studied experimentally. If interface catalysis were proved in either of these

reactions, a specialised mechanism may legitimately be assumed.

My thanks are due to Mr. A. C. G. Egerton for his criticism of this communication.

#### Summary.

The cases of interface catalysis so far discovered in the reduction of metallic oxides seem to be due to the difficulty in forming any intermediate stage in the reduction. No other mechanism need be assumed.

<sup>6</sup> Pease and Taylor, J.A.C.S., 43, 2179, 1921. Cf. reduction by CO, Jones and Taylor, J. physical Chem., 27, 623, 1923.

<sup>7</sup> Cf. lecture by Professor Ingle Finch to the Chemical Society, November, 1932.

Clarendon Laboratory, Oxford.

#### REVIEWS OF BOOKS.

The Sorption of Gases and Vapours by Solids. By JAMES WILLIAM McBain, F.R.S., Professor of Chemistry at Stanford University, California. (London: George Routledge & Sons, Ltd. 577 + xii pages with 151 diagrams. Price 25s. net.)

There have been so many books on adsorption that the need for another was not apparent until Professor McBain's book actually appeared. An authoritative exposition of any subject is always welcome, especially when it embodies a point of view gathered in the course of many years' research. From another angle

also, the book is of interest, for it reveals the personality that has carried out a very systematic series of researches in Colloid Chemistry.

From a perusal of the book, it is clear that to Professor McBain, the body of science is composed of facts, with no more than a sufficiency of theory to make them cohere. It is not a large book, and yet it contains a reference to practically every research published on adsorption. In reading the book one often appreciates the occurrence of unfamiliar facts in their place in an orderly description of some of the phenomena of adsorption. It is a remarkable achievement to have "boiled down" so much material into a readable book of less than 600 pages.

The author divides the book into three parts, (I) an introduction on the historical aspect and experimental methods, (2) experimental data, and (3) hypotheses and theories of sorption. By far the most important section is that on experimental data, which comprises two-thirds of the book. The facts are summarised on a plan which very readily facilitates reference. They are mainly grouped in chapters dealing with the various types of material used as adsorbents, for example, charcoal, zeolites, porous rigid jellies, glass, impermeable crystals, metals, cellulose derivatives, etc. Facts applicable to some or all of these types are grouped under headings concerning the nature of the surface of adsorbents and adsorbed films, the effect of sorption on the solid, the heat of adsorption, and the mobility in surface films. In the main, the vast range of material is discussed from the point of view of the better established theories of adsorption, but the researchers' opinions with regard to their own work are not ignored, although in appropriate instances, Professor McBain gives his own opinion as to the explanation of the phenomena described. This makes the book a human document and not a mere collection of facts.

The hypotheses and theories of capillary condensation, thick compressed films, monomolecular adsorption, contact catalysis and various electrical theories are discussed in the third section of the book. The essential features of these theories are clearly presented, the discussion on the Langmuir and Polanyi theories being especially valuable. The treatment is not very mathematical and not at all wave mechanical. It is sufficiently simple to be read with advantage by University students.

There are minor points of criticism, which concern the relative importance of various lines of attack on the problems of adsorption, about which each worker on adsortion has very definite opinions. Very little attention is paid in the book to the adlineation theories, the theories of Stranski, the effect of environment of surface atoms on their adsorption capacities, Smekal cracks and their bearing on adsorption, and the mobility of molecules adsorbed on the surfaces of metals. One inclines to the opinion that the book would have been more valuable had these aspects been more fully discussed.

The reader becomes accustomed to the absence or presence of a particular prefix before the word "sorption," but nevertheless wonders if a classification which is almost entirely based on the structure of the adsorbent will prove so useful in the long run as one based on the nature of the forces binding an adsorbed molecule to a surface.

The author has succeeded in producing a textbook on adsorption which will serve a dual purpose. It is a very valuable work of reference and at the same time is a textbook suitable for student use.

The Method of Dimensions. By Professor A. W. Porter, D.Sc., F.R.S. (London: Methuen & Co., Ltd., 1933. Pp. v + 78.)

In any matter that appears over the signature of Professor A. W. Porter one instinctively looks for high qualities of scholarship and subtlety, with, on occasion, a certain measure of provocativeness. Readers of this fascinating little volume, which, as the author reminds us, is the first of its kind to appear in English, will not be disappointed. The volume opens with a chapter on general considerations, occupying some eleven pages. We could wish that this had been doubled in length, for there are many delicate and difficult points in the general development of the theory concerning which a detailed treatment would have been very valuable. In particular, we should have welcomed a statement of Professor Porter's views concerning the attitude taken by Dr. Campbell in his book on Measurement and Calculation. In the succeeding chapters the author gives a succinct and learned discussion of the application of dimensional analysis to problems dealing with the flow of fluids, surface tension, vibrating systems, temperature and heat effects, and electricity and magnetism.

Truly, infinite riches in a little room!

A. F.

Comprehensive Treatise on Inorganic and Theoretical Chemistry. By J. W. Mellor, D.S.C., F.R.S. Volume XII. U, Mn, Ma, Re, Fe (Part I.). (London: Longmans, Green, & Co., 1931. Pp. xii + 944. £3 3s. net.)

One of the most interesting sections of this volume is that devoted to the "younger generation" of elements, Masurium and Rhenium, whose discovery and investigation fall within the last decade. Owing to their rarity, their study needs a high degree of manipulative skill, and it is gratifying to find that much pioneer work is being done in this country. Each forms about one thousand millionth of the total number of atoms in the earth's crust and one cannot help wondering whether the future will find these elements exploited commercially like the so-called rare gases. Rhenium appears to have a melting-point as high as, or higher than, that of tungsten. Uranium occupies 138 pages and maganese 326. The radioactivity of the former element is not here discussed, but in Volume IV. Manganese is very versatile chemically and it has therefore always been the subject of much investigation. It is perhaps somewhat astonishing to find that 28 pages are needed to deal with potassium permanganate; the physical chemist has here found much to study.

About half the volume is devoted to the history of the use of iron, the manufacture of the various forms of iron and steel and the properties of the iron-carbon alloys. This section thus forms one of the most considerable and most modern surveys of this field of knowledge. The treatment is very lucid and readable.

The volume contains a list of errata for previous volumes; these average four per volume—a remarkable tribute to all concerned in the production of this monumental work.

C. H. S.

## GLASS ELECTRODE DETERMINATION OF THE DISSOCIATION CONSTANT OF HYPOCHLOR-OUS ACID.

By H. T. S. BRITTON AND ERIC NORMAN DODD, Ph.D.

Received 25th July, 1932.

The determination of the dissociation constant of hypochlorous acid has been a problem of some difficulty. Nernst 1 and W. A. Noves and Wilson 2 found that conductivity measurements of stationary solutions are vitiated by the decomposition of the hypochlorite which occurs at the electrodes, but by using flowing solutions the latter workers claim to have obtained accurate data, from which they calculated 3 that  $K = 6.7 \times 10^{-10}$  at 25°. The only other determinations of the dissociation constant are based on indirect methods, viz., (I)  $3.7 \times 10^{-8}$  at 17°, found by Sand <sup>1</sup> from the solubility of carbon dioxide in sodium hypochlorite solutions; (2) I × 10-8 at 25° obtained by Soper 3 using a vapour pressure method. None of the values hitherto obtained result from direct measurements, which in all probability can only be made by the glass electrode.

## Experimental.

The glass electrode apparatus, previously employed by Britton and Robinson 4 was used to titrate 100 c.c. of 0.027 N sodium hypochlorite solution with 0.252 N sulphuric acid at 15° C. Reproducible curves were obtained. Table I. gives the pH values and pK values corresponding to the various stages of the titration :--

TABLE I.

Equivs. H <sub>2</sub> SO <sub>4</sub> . Equivs. NaClO	0.122	0.220	0.375	0.500.	0.625.	0'750.	0.875.
<i>Р</i> в · · · · · · · · · · · · · · · · · · ·	8·40	8·00	7·72	7·50	7·27	7:00	6·61
	7·55	7·52	7·50	7·50	7·49	7:48	7·46

Mean value of  $p_{K_{\text{HClO}}}$ : 7.50.

The sample of sodium hypochlorite used contained a certain amount of sodium chloride, and it was considered advisable to examine the

<sup>&</sup>lt;sup>1</sup> Cited by Sand, Z. physikal. Chem., 46, 610, 1904. <sup>2</sup> J. Amer. Chem. Soc., 44, 1630, 1922. <sup>3</sup> See, however, Soper, J. Chem. Soc., 2227, 1924. <sup>4</sup> Trans. Faraday Soc., 27, 531, 1932.

effect, if any, of this neutral salt upon the  $p_{\rm H}$  values of partially neutralised solutions of hypochlorous acid, and therefore on the dissociation constant of the acid. To this end, solutions of hypochlorous acid were prepared by shaking chlorine water with precipitated mercuric oxide and then distilling, when a solution of the pure acid was obtained as distillate. The purity of the distillate was rectified by shaking with silver nitrate solutions; only the merest opalescence was observed. Titrations of 100 c.c. of 0.063 N hypochlorous acid with 0.20 N sodium hydroxide yielded reproducible curves, the data of which are quoted in Table II. Similar titrations were then carried out on solutions of hypochlorous acid containing varying amounts of sodium chloride, and the figures show the effect of the neutral salt on the  $p_{\rm H}$  to be negligible.

Mean Conc. Equivs. NaClO 0.500. 0.625. 0.750. 0.875. of NaCl. 0.122. 0.250. 0.375.  $^{p}$ KHCIO. Equivs. HClO  $p_{\mathrm{H}}$ 8.40 6.58 8.01 0.0 7.00 7.27 7.50 7.74 7.43 7:45 7.49 7:50 7.52 7:53 7:55 7:50  $p_{\rm H}$ 6.62 6.95 7.50 8.01 8.38 0.10 7.25 7.73 7.47 7.43 7.47 7:50 7:51 7:53 7.53 7.49  $p_{\rm H}$ 6.60 6.95 7.70 7.97 8.33 0.25 7.21 7.45 7.45 7.48 7.48 7.46 Þ 7.43 7.45 7.49 7.43

TABLE II.

The concentration of sodium chloride is expressed in gram-molecules per litre.

The dissociation constant of hypochlorous acid is therefore  $3.2 \times 10^{-8}$  at 15° C. ( $p_K = 7.50$ ).

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## DISCONTINUITIES AND THE NATURE OF ADSORBENT SOLIDS.

By G. H. PIPER.

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Many adsorption isotherms formerly believed to be smooth curves have been found to exhibit discontinuities on more careful investigation. The systems investigated which exhibit this behaviour are benzene, carbon tetrachloride, water and other condensible vapours on charcoal, water and carbon tetrachloride on silica gel by the retentivity method, <sup>2</sup>

<sup>&</sup>lt;sup>1</sup> Allmand and Burrage, *Proc. Roy. Soc.*, **130A**, 610, 1931. <sup>2</sup> Burrage, *J. Physic. Chem.*, **35**, 1692, 1931.

nitrogen and hydrogen on various metal adsorbents <sup>3</sup> at — 183° C., and hydrogen on charcoal at 0° C.<sup>4</sup>

In all these systems except the last, the adsorption is of the easily reversible, non-specific type characteristic of Van der Waals or physical adsorption. Though these phenomena still require further confirmation and experimental investigation, it is probable that the explanation based on Semenoff's treatment of surface equilibria 5 is the true one. gases below their critical temperature, the lateral attraction between adsorbed atoms may reach a critical value, resulting in the transition of the adsorbed atoms from the two dimensional gaseous state to the close packed liquid state. This transition occurs at a critical value of the pressure determined by the temperature and potential of the surface. In the case of a composite surface possessing regions of different adsorptive power, the adsorbed substance will be spread over the surface in the form of discontinuous islands of liquid, the transition of a patch from the two dimensional liquid to the gaseous state resulting in a discontinuity on the adsorption isotherm. A modified interpretation put forward avoids the assumption as to regions of different adsorptive power by assuming that adsorption starts out from active centres from which islands of sorbate, of the close packed type, spread out. An island is considered as composed of concentric rings, the completion of a ring and the commencement of a new one being marked by a break.

While an explanation on these lines appears adequate for those systems in which vapours are involved, it cannot be applicable to the other systems in which the temperature is far above the critical temperature of the gas involved. These systems are hydrogen on charcoal  $^4$  at 0° C., hydrogen on active copper  $^3$  at - 183° C., and hydrogen on charcoal  $^6$  at - 183° C. In all these cases the temperature is too high for the formation of two dimensional liquid patches of the type discussed above—the critical temperature of hydrogen being - 241° C. Discontinuous behaviour is shown in all three cases, the adsorption isotherm for the first two being of a jagged or steplike nature, while that investigated by Ubbelohde shows abrupt decreases in slope with increasing pressure.

It is suggested here that these discontinuities obtained with permanent gases are different in their nature from those investigated by Allmand and Burrage in which easily condensible vapours were involved. If this is the case, a different explanation must be put forward to account for the existence of this other type. A possible explanation is that the surface of the adsorbent may consist of regions of different adsorptive power, but there is no a priori reason to suppose that these regions are not distributed about a mean value. In the mechanism outlined below, it is suggested rather that these discontinuities are a consequence of the peculiar internal structure of many adsorbent solids, due to their extremely large specific surface.

The majority of adsorbing substances require special activating treatment before they acquire good adsorptive powers. This is especially the case with metals, which with a few exceptions, show poor adsorbing properties when in the normal state. In general, they are prepared in the active condition by reduction of the oxide with hydrogen, action of heat on the metallic tartrate, etc., and it would seem that the mechanism

<sup>&</sup>lt;sup>3</sup> Benton and White, J.A.C.S., **53**, 3301, 1931. <sup>4</sup> Schuster, Trans. Faraday Soc., **28**, 275, 1932.

<sup>&</sup>lt;sup>5</sup> Semenoff, Z. physik. Chem., 7B, 471, 1930.

<sup>6</sup> Ubbelohde and Egerton, Proc. Roy. Soc., 134, 512,

consists essentially of the production of metal atoms in an almost isolated condition, followed by an only partial sintering to form a coherent structure. The metal lattice thus formed would necessarily be an imperfect one, it would be distorted, there would be numerous crevices and breaks. Active copper can also be prepared by exposure of the metal to ammonia at a high temperature, its physical properties are then much altered. While copper en masse has little or no adsorptive power and is almost non permeable to hydrogen, when heated to 600° C. hydrogen is able to diffuse through, the rate increasing at first even though the temperature and pressure are kept constant. At the same time changes in the copper take place—it becomes brittle after a time and its adsorptive powers are found to have increased. It seems difficult to resist the conclusion that the hydrogen in diffusing through the copper has actually entered into the metal lattice, distending it and breaking it in places where the strain is greatest. Presumably the activating effect of ammonia is caused by a similar penetration. In this connection also there is the investigation by Rupp of metal surfaces by electron beam reflection.8 By using electron beams of low voltage the effect of even a monomolecular layer of hydrogen gas on the reflection diagram of the metal surface can be clearly observed. With many metals, including nickel, copper and iron, the effect of the gas is to introduce new maxima between the maxima due to the metal itself. Thus the first atoms of gas adsorbed on the {III} surface of a clean nickel crystal arrange themselves in a similar structure but with twice the scale factor. Prolonged exposure to the hydrogen, or brief heating, causes a broadening and lessening of the maxima due to the surface nickel atoms and intensifies those due to the hydrogen. This was interpreted as an opening up of the exterior of the space lattice. Similar effects are observed with iron and copper surfaces.9 Thus it would seem that the adsorbing properties of a metal in the active as compared with the normal condition are to be attributed to the opened out nature of the lattice and the consequent acquisition of what may be termed a molecular porosity, so that hydrogen and gases of not great molecular diameter are able to penetrate. It is possible that a slow penetration into such an opened out lattice may account for the existence of activated adsorption. Richardson, 10 who investigated the diffusion of hydrogen through platinum, found that the rate was given by an expression of exponential form

$$D = KP^{\frac{1}{2}}T^{\frac{1}{2}}e^{-\frac{q}{4}T},$$

where D is the diffusion constant and T the absolute temperature. This expression applies also to the diffusion of hydrogen, nitrogen and carbon monoxide through steel.

In the case of these active adsorbents, possessing what may be termed molecular porosity, it does not seem possible to speak of them as possess-

Soc., 28, 144, 1932.

<sup>&</sup>lt;sup>7</sup> Lombard, J. chim. physique, 25, 590, 1928; Deming and Hendricks, J.A.C.S.,

<sup>45, 2857, 1923.

8</sup> Rupp, Z. Electrochem., 35, 586, 1929; Ann. Physik (5), 5, 453, 1930.

9 This work would seem to lead to interesting developments in connection with catalytic reactions. If the effect of hydrogen is to open up the top layers of the metal lattice, then in certain reactions on metal surfaces the reacting gases will be able to penetrate to a certain extent, if their molecular diameters are small. Thus the reaction will partly take place within the metal lattice to a depth of perhaps two or three lattice spacings below the surface.

10 Phil. Mag. (6), 7, 266, 1904; 8, 1, 1904. See also Rideal, Trans. Farad.

ing a definite surface. While the latter term may be convenient for the discussion of adsorption theory, its retention in the case of these active adsorbents seems to be misleading. Thus it comes as a surprise to many investigators who have retained the classical picture of adsorption on a surface to find that the dimensions of many adsorbents undergo an appreciable increase during the process of sorption.

Activated charcoal has features in common with these metal adsorbents and it is convenient to discuss its structure in relation to discontinuities. Adsorption in this case is closely related to the presence of carbon atoms which have their valencies incompletely saturated and which thus have a strong tendency to form complexes with gas molecules. In the form of diamond, the symmetrical arrangement of the carbon atoms in the crystal lattice ensures the saturation of each of the four valencies and also that the angle between adjacent bonds shall be the angle of least strain—110°. Charcoal, on the other hand is non-crystalline, and if, as is probable, the carbon atoms are arranged almost haphazard, must be in a state of internal strain due not only to the incomplete saturation of the four valencies but also the distortion of the carbon-carbon bonds from out of the angle of least strain. Charcoal in many ways retains the appearance of the wood from which it has been prepared and it has been concluded that the long parallel chains of carbon atoms constituting the cellulose structure remain practically intact during the process of carbonisation.11 The spaces between adjacent chains constitute capillaries of diameters extending upwards from molecular dimensions, in which gases may be adsorbed on the unsaturated carbon atoms.

While the unsaturated nature of these exposed carbon atoms may be relieved by their adsorbing gas molecules, it is probable that, even in the absence of gas, carbon atoms specially situated on opposite sides of the capillary may temporarily relieve their unsaturated nature by forming a link between themselves. Whether such links are readily formed or not will clearly depend on the capillary diameter. Since the capillaries vary in diameter, such links will in general have widely different stabilities. The energy required to break such a link, which is a measure of the stability of the link, will depend on the distance apart of the atoms and can probably be represented approximately by a curve of the London type. 12 For a certain distance apart (equilibrium distance) this energy will be a maximum. For larger distances apart, the energy will be less and the force required to separate the atoms smaller. Links of the first kind will be stable and form a permanent part of the structure. It is the links of the second kind, and especially those which require little energy to break and are thus unstable, which interest us here, since it is these links, uniquely situated at certain parts of the capillaries. which are believed to give rise to the discontinuities observed.

The admission of a gas to an evacuated charcoal containing links of this type will to a large extent affect their stability. The adsorption of a gas is in general accompanied by an expansion of the solid and, in addition to the mechanical pressure exerted by the gas on the walls of the capillary, the adsorption of gas on carbon atoms and the resulting valence change of these unsaturated atoms will profoundly affect the stability of any labile links in the immediate vicinity. While the actual number of links of an unstable type is large, so that the energy distribution curve is a smooth one, it is only at certain parts of the adsorbent

Lamb, Wilson and Chaney, J. Ind. Chem., 11, 429, 1911.
 Naturwiss., 26, 516, 1929.

that the links will be so grouped together that the ordinary rigidity of the adsorbent is affected, so that a simultaneous breakage of many links is possible and a violent rearrangement of the surface in the vicinity follows, so as to release the surface strain. Such a rearrangement may be a widening of the capillary diameter or an opening out of a hitherto inaccessible part of the structure, thus the adsorption isotherm will no longer be smooth but will exhibit discontinuities where such abrupt breaks have taken place. That such alterations in the surface take place occasionally during the process of adsorption or desorption have been known for some time—e.g. Berliner 13 has found that the removal of adsorbed gas from active metals by evacuation is often accompanied by a partial sputtering of the surface; in general such alterations are especially probable in the case of adsorbents of marked non-rigid character. such as charcoal. In an active charcoal the effective surface or rather the accessibility of the interior has been so increased that one molecule of gas may be adsorbed per nine atoms of carbon, from which it follows, on the assumption that one molecule is adsorbed on two carbon atoms, that the wall atoms of charcoal constitute 25 per cent. of the whole. Such a loose structure would be expected to be especially susceptible to the influence of adsorbed gas. Discontinuities produced by the above mechanism would not be expected to be reversible. The experimental work at the present time appears to be insufficient to enable a decision to be made on this point.

The case of charcoal has been discussed in detail because of the more definite state of knowledge of the homopolar bonds operative between the carbon atoms, but a similar behaviour will be expected from other adsorbents having the same type of semi-rigid structure. Metals in the active condition will contain similar links of an unstable nature.

Discontinuities of the above type should clearly be reflected in other properties relating to the adsorbent. Most adsorbents, especially those exhibiting molecular porosity, increase appreciably in volume during the process of sorption, owing to the distension of their structure. With charcoal this linear increase is of the order, 0.2 per cent. per atmosphere in the case of carbon dioxide, but no measurements have been made with a view to ascertaining whether this increase is discontinuous in any way. The dimensions of palladium increase considerably during the sorption of hydrogen, and Harding and Smith, who investigated the linear increase in a fine palladium wire, detected what they termed fluctuations in this property during the sorption process. 14 The hydrogen was produced electrolytically on the palladium and the maximum increase in length was about 3 per cent. The resistance of the wire was observed simultaneously, and fluctuations in resistance observed were found to coincide with the fluctuations in length. Further work of interest in connection with the above views and of an entirely different nature is that by De Forest on metal wires. 15 De Forest studied the plastic elongation of metal wires produced by the application of external forces, using an apparatus which recorded automatically the stress strain diagrams on sensitised paper. While some metals gave smooth curves, others were found to give curves of a jagged type, the discontinuities becoming more pronounced with rise of temperature. Some of these diagrams strongly resemble some discontinuous adsorption isotherms.

<sup>13</sup> Wied. Annal. Physik., 33, 289, 1888.

<sup>&</sup>lt;sup>14</sup> J.A.C.S., **40**, 1508, 1918.

<sup>&</sup>lt;sup>15</sup> Proc. American Society of Testing Materials, (2), 468, 1916.

the precise interpretation of these diagrams is not altogether clear, the work is of interest since (I) it shows that a solid by itself may exhibit a discontinuous change in one of its properties, (2) there is a clear analogy between the strained metal and an adsorbent distended internally by adsorbed gas.

The energy change involved in the rupture of a carbon link is approximately 137,500 cals., 16 and that of a link in an unstable condition will be somewhat less. The heat of adsorption of a gas molecule on two carbon atoms previously united by an unstable link will thus be less than the normal heat of adsorption owing to the breakage constituting an endothermic change. Several cases are known in which the differential heat of adsorption has a low initial value at low pressures rising rapidly to a maximum and then falling slowly.<sup>17</sup> This low initial value is difficult to explain. It has been interpreted by various observers as a dissociation of the adsorbed molecules on the active spots. this explanation appears a possible one for the systems, hydrogen and copper, and perhaps also oxygen and nitrous oxide on charcoal, it does not seem applicable to the system carbon monoxide on copper, which, like the others, gives a low initial value of the differential heat. By making the assumption, however, that the initial quantities of carbon monoxide are adsorbed by the mechanism described above, with the simultaneous breakage of unstable links, the low value of the initial heat of adsorption is explained without recourse to any assumption involving dissociation of the molecule, an assumption that in the case of carbon monoxide would be opposed to experimental facts. Though the precise nature of the inter-atomic forces in metals is still a matter for discussion, the energy of such linkages is at least of the same order as the energy of covalent bonds of the carbon carbon type. The heat of vaporisation, which is the energy required to remove an atom from its neighbours to an infinite distance, is for copper of the order 50,000-100,000 cals. per gram atom (that of carbon, representing the breakage of two links, is 287,000 cals.) From the quantitative view, the energy relation of the atoms in a metal surface and the effect of adsorbed gas molecules are problems to be eventually solved by the methods of wave mechanics.

## Summary.

Discontinuous adsorption isotherms are discussed. It is shown that the theory involving the transition of the adsorbed layer from the two dimensional gas to the liquid state is not applicable to all the cases observed. A new mechanism is put forward, based on the assumption of labile links present throughout the adsorbent. The assumption is further found to lead to a satisfactory explanation of low initial values of heats of adsorption.

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<sup>&</sup>lt;sup>16</sup> Fajans, Ber., **538**, 643, 1920.
<sup>17</sup> Bull and Garner, Nature, **124**, 409, 1929; Cameron, Trans. Farad. Soc., **26**, 239, 1930; Taylor, Z. Electrochem., **35**, 542, 1929; Taylor and Kistiakowsky, Z. physik. Chem., **125**, 341, 1927.

## THE THERMAL DECOMPOSITION OF LEAD STYPHNATE.

By H. R. Hailes.

Received 11th Fanuary, 1933.

Crystals of lead styphnate, C<sub>6</sub>H(NO<sub>2</sub>)<sub>3</sub>(OH)<sub>2</sub>PbO, lose water on being heated to 120° C. in a vacuum and "the dehydration causes no change in the shape and clarity of the crystal." At temperatures above 200° C. the water of crystallisation is lost very rapidly, and the crystals become broken into fragments. Thermal decomposition follows the dehydration, and if the temperature be over 225° the decomposition passes into detonation. The study of the mode of thermal decomposition of this explosive is of interest, since, owing to the loss of water, the crystals possess a large internal surface.

The thermal decomposition of solid substances usually commences at centres formed on the external surfaces, the edges, and the corners of the crystals, but this is by no means universally true. Crystals of B-lead azide and mercury fulminate, as microscopical examination shows, undergo decomposition within the crystal boundaries, the products of decomposition escaping along microscopical and submicroscopical cracks.<sup>2</sup> Three stages can be distinguished in the decomposition of fulminate: (I) a quiescent period during which little gas is produced,3 (2) a period of acceleration during which the rate of reaction is given by the logarithmic law,  $\log (dp/dt - dp_0/dt) = k_1t + \text{const}$ , and (3) a final stage when the rate obeys the law for reactions of the first order. By way of explanation of these facts it was suggested that the reaction starts in the unorganised matter along the Smekal cracks and then spreads around the crystallites until by the time of half decomposition the latter are completely separated from one another by decomposition products. The second stage in the reaction is considered to correspond to the spread of the decomposition around the crystallites by a chain mechanism, and the third stage to consist in the decomposition of the isolated grains in which the unimolecular law is obeyed because the rate is determined by nucleus formation.4 Ground and crushed fulminate shows no quiescent period, and the decomposition occurs in two stages The present investigation has shown that lead (2 and 3 above). styphnate behaves like crushed and ground fulminate.

## Experimental.

The method employed in the study of the thermal decomposition of lead styphnate has been described previously.<sup>2</sup> Single crystals were used, 0.5 to 5.0 mgm. in weight. These were kindly supplied by Messrs. Nobel's Explosives Co. Ltd. They were suspended in vacuum at the

 $<sup>^1</sup>$  Miles, J.C.S., 1931, 2541.  $^2$  Garner and Gomm, J.C.S., 1931, 2123; Garner and Hailes, Proc. Roy. Soc., communicated.

<sup>&</sup>lt;sup>3</sup> Farmer, J.C.S., 121, 174, 1922. 4 Cf. Hume and Colvin, Phil. Mag., 8, 589, 1929.

required temperature and the pressure changes followed by means of a McLeod and a Pirani gauge. The Pirani gauge was calibrated against

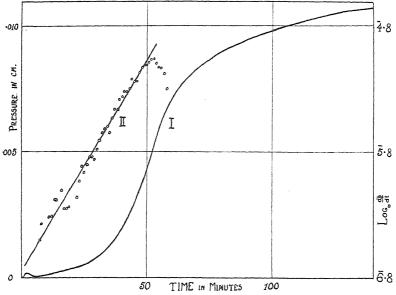


Fig. 1.—Thermal Decomposition of Lead Styphnate.

the McLeod, using the gases produced in the decomposition after water vapour had been removed. The volume of the apparatus including

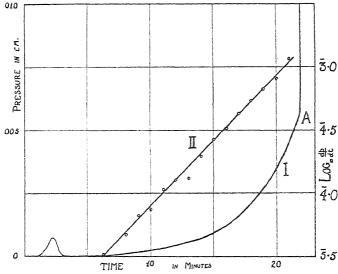


Fig. 2.—Thermal Decomposition Leading to Detonation.

gauges was 909 c.c. Before each experiment the apparatus was evacuated for twenty-four hours with the crystal and bucket at room

temperature. The water evolved on heating was removed in an appendix immersed in solid carbon dioxide and alcohol. A typical curve showing the pressure change with time is seen in Fig. 1, curve 1. The small maximum on this curve is due to the evolution of water of crystallisation which is not condensed as rapidly as it is formed.

#### Results.

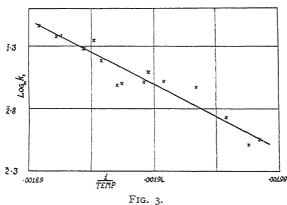
## Thermal Decomposition.

After the crystal has given up its water of crystallisation, the decomposition begins to accelerate. Curves II in Figs. 1 and 2 show the plots of log  $\mathrm{d}p/\mathrm{d}t$  against t, for thermal decomposition and for a case where detonation occurred. It is seen that the same law holds for styphnate as for fulminate, viz: log  $(\mathrm{d}p/\mathrm{d}t - \mathrm{d}p_0/\mathrm{d}t) = k_1t + \mathrm{const}$ . In the case of styphnate, however,  $\mathrm{d}p_0/\mathrm{d}t = \mathrm{o}$ . The following table gives the values of  $k_1$  and the integration constants obtained when  $\mathrm{d}p/\mathrm{d}t$  is expressed in cm./min.:—

Temp. °C.	k <sub>1</sub> .	Constant.	Temp. °C.	k <sub>1</sub> .	Constant.
225 231·5 232·5 235 238 241·5 243 243·5	0.0087 0.036 0.033 0.054 0.094 0.105 0.125	8.024 × 10 - 8 3.1 7.5 8.1 5.2 8.8 1.8 7.0	246 246·5 248 249 250 252·5 253 255	0·126 0·097 0·153 0·223 0·191 0·243 0·238 0·289	3.5 × 10 - 6 1.3 × 10 - 5 4.9 × 10 - 6 5.2 3.8 4.4 2.1 9.7

TABLE I.

The plot of  $\log k_1$  against 1/t is given in Fig. 3. From the slope of the



best straight line, as drawn, a critical increment of 46,700 cals. is obtained. The integration constants are of the same order as those obtained with crushed and ground fulminate.

It is seen from Fig. 2 that the acceleration law holds right up to the point at which detonation occurs

(A), and this is true in all cases where detonation takes place. When no detonation occurs, the law holds up to 50 per cent. decomposition. After that, as with fulminate, the reaction obeys the unimolecular law:

$$\frac{1}{t}\log\frac{p_f}{p_f-p_t}=k_2,$$

(where t is taken as the time from some zero point determined by extrapolation and  $p_t$  is the pressure at time t, and  $p_t$  that at the end of the reaction). The degree of constancy obtained is shown by the following values for a crystal at  $232 \cdot 5^{\circ}$  C.:—

Time 60 70 80 90 101 114 120 
$$k_2$$
 0.0136 0.0142 0.0146 0.0142 0.0144 0.0138 0.0173

The values of  $k_2$  were only obtained in a few cases,\* which are given in Table II.

#### Time to Detonation.

The times which elapse before detonation occurs are shown in Table III for the range of temperatures 225°-255° C.

The figures in Column III show that these times are not very reproducible, but a fairly good straight line can be drawn

#### TABLE II.

Temp. °C.	k <sub>1</sub> .	$k_2$ .
231·5	0·036	0·030
232·5	0·033	0·014
250	—	0·0046

through the experimental points obtained by plotting log time against 1/t. This is shown in Fig. 4. The critical increment obtained from the slope of this line is 39,000 cals. There is more uncertainty in this figure than in the values obtained with mercury fulminate.

TABLE III.

Temp. °C.	Weight of Crystal. (mgm.).	Time to Detonation. (mins.).	Temp. ℃.	Weight of Crystal. (mgm.).	Time to Detonation. (mins.).
225 227 235 238 239 241 241·5 241·5 243	4·696 6·756 1·050 1·463 0·855 0·932 1·511 1·744 1·436	81:4 22:5 35:9 22:9 25:9 20:8 17:0 21:2	243.5 246.5 246.5 248 249 250 250 252.5 253	0.692 0.679 0.459 0.971 1.581 0.545 0.987 1.716 0.828	21·8 19·5 19·6 14·4 9·5 13·1 9·2 9·2 12·4 8·2

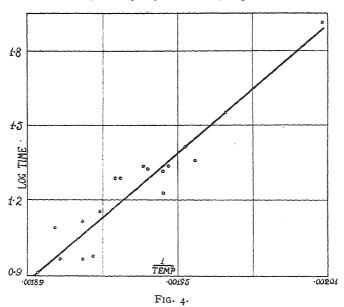
In this case, as in the case of fulminate, the effect of size is partly responsible for the lack of reproducibility of the results, although the pulverisation of the crystal on the liberation of water may be responsible for part of the trouble. The following table shows that small crystals undergo thermal decomposition at temperatures for which detonation occurs with larger crystals:—

<sup>\*</sup> The applicability of this equation, which was worked out for fulminate crystals, was not tested in the case of styphnate, until their investigation had been completed. Only a few experiments had been carried out to the stage of complete decomposition. Logarithms are to base 10 in all cases.

TABLE IV.

Thermal De	composition.	Detonation.				
Temp. °C.	Weight in mgm.	Temp. °C.	Weight in mgm.			
229 231·5 232·5 240·8	2·205 1·449 0·634 0·756	225 227	4·696 6·756			

The crystals which detonated at 225° and 227° C. were unusually large-crystals. A more detailed study of the results shows that all those-crystals which give high values for the time to detonation (taking the normal value as being given by the line in Fig. 4) weigh less than I mgm., and low values are given by crystals of 1.5 mgm. and over. Thus it



seems that in this case even more than in the case of fulminate crystals of a standard size should be adhered to.

The detonation of styphnate crystals does not occur outside the period of acceleration of the reaction.

#### Discussion.

From the foregoing results, it is evident that the thermal decomposition of lead styphnate monohydrate involves three processes:

- (1) The break-up of the crystal with the evolution of water,
- (2) The acceleration of the reaction, governed by the law:

$$\operatorname{Log} dp/dt = k_1 t + \operatorname{const.},$$

(3) The falling off of the rate of decomposition, according to the unimolecular law:

$$1/t \{ \log p_f / (p_f - p_t) \} = k_2.$$

The second and third processes are the same as for fulminate. The reaction which occurs during the period of acceleration can be explained in terms of a branching chain mechanism. If  $N_0$  is the number of chains started per minute and N the number of chains in existence at any time, and K is the probability of branching,

then

$$\log_e N = \log_e \frac{N_0}{K} + K_1 t$$
$$= Kt + \text{constant.}$$

Under certain conditions, which are fulfilled in this case,  $\mathrm{d}p/\mathrm{d}t$  is proportional to N; therefore  $\log \mathrm{d}p/\mathrm{d}t = k_1t + \mathrm{constant}$ . As is the case for fulminate, the critical increment of  $k_1$  must be that of the branching process. This was found to be 46,700 calories.

The locus of the reaction chains is uncertain in the case of lead styphnate. If the process of dehydration of the salt be analogous to that which occurs in a zeolite, as is maintained by Miles,\* then the chains probably start in the channels along which the water molecules have escaped, and penetrate throughout the mass. If, on the other hand, the pseudomorph has a structure analogous to that of dehydrated copper sulphate 5 then the explanation previously given for fulminate can be applied to the case of lead styphnate. This question will be further discussed in a later paper.

## Summary.

Lead styphnate undergoes thermal decomposition above 200° and detonates above 225° C. The thermal decomposition obeys the same laws as crushed and ground mercury fulminate. During the period of acceleration the reaction obeys a branching chain mechanism.

I wish to express my indebtedness to Nobel's Explosives Co. Ltd. for a personal grant which has made this work possible.

The Physical Chemistry Department, The University, Bristol.

<sup>\*</sup> Private communications.

<sup>&</sup>lt;sup>5</sup> Cf. Topley, Proc. Roy. Soc., 136A, 413, 1932.

# THE COPPER-MAGNESIUM ALLOYS EXAMINED THERMODYNAMICALLY.

By F. H. JEFFERY.

Received 11th January, 1933.

Recently W. R. D. Jones <sup>1</sup> has given a thermal equilibrium diagram of these alloys which he obtained by thermal and micrographic analysis. He found that the liquidus has two maxima corresponding to the compounds MgCu<sub>2</sub> and Mg<sub>2</sub>Cu, that there are three eutectics at 722°, 552° and 485°, that there are solid solutions of magnesium in copper and of copper in magnesium, but that the two compounds do not form solid solutions. He found no evidence of the existence of MgCu in the solid state. He used re-distilled magnesium of purity 99·99 per cent. and electrolytic copper of at least 99·99 per cent. purity.

It seems interesting to examine the molecular constitution of the liquid and solid solutions, the latter being of importance, since in some cases the results of thermodynamic analysis are not consistent with the results obtained by X-ray analysis; examples of this inconsistency are given by the solid solutions  $Cu_4Sn$  in Cu,  $CuZn_4$  in Cu,  $Pb_2Sb$  in Pb,  $Cu_3Sn$  in Sn,  $CuZn_2$  in Cu, these being the constitutions as given by the author's method. None the less, the X-ray method applied to the solid state cannot be less fundamental than thermodynamics applied to the same distribution.

The following calculations are based on the work of W. R. D. Jones, using the atomic weights Cu = 63.57, Mg = 24.32.

(i) For the portion of the liquidus between 1083° C. and the eutectic at 722° C, and for the corresponding portion of the solidus the boundary conditions can be satisfied if both liquid and solid solutions consist of monatomic molecules of magnesium dissolved in monatomic molecules of copper. The equation must be of the form

$$-\log(1-n) + \log(1-n') = \lambda/R\theta - \lambda/R\theta_0,$$

n and n' being the molal fractions of the solute; for concentrations for which  $\lambda$  is sensibly constant,  $-\log(1-n)+\log(1-n')$  must be a linear function of  $1/\theta$ . The results shown in Table I were obtained:—

TABLE I.

θ.	p.	<i>p</i> ′.	<b>5</b> 1.	n'.	$-\log(1-n) + \log(1-n').$	1/θ.
1356 1343 1333 1323 1313 1303 1293	0·50 0·80 1·14 1·47 1·80 2·10	0·10 0·16 0·23 0·30 0·37 0·42	1·30 × 10 <sup>-2</sup> 2·06 2·93 3·75 4·57 5·31	2·61 × 10 <sup>-3</sup> 4·02 5·99 7·80 9·62 10·9	0·0 0·0046 0·0073 0·0103 0·0132 0·0161 0·0189	7·374 × 10 <sup>-4</sup> 7·446 7·502 7·559 7·616 7·675 7·734

<sup>&</sup>lt;sup>1</sup> W. R. D. Jones, J. Inst. Metals, 46, 395, 1931.

These points lie close to the straight line through the first and the fourth. The assumption as to the constitutions is therefore justified. The mean value of  $\lambda = 2.31 \times 10^3$ .

(ii) There seems to be no reason to assume any discontinuity of the liquid phase for concentrations from that of the eutectic at 722° to that corresponding with the compound  $\rm MgCu_2$ . As the liquid alloys freeze the reaction must be :  $\rm Mg + 2~Cu = MgCu_2$ , and the form of the equation that satisfies the boundary conditions must be

$$-\log n - 2\log(1-n) = \lambda/R\theta + \text{const.}$$

The results shown in Table II were obtained. These points lie close

 $+\log n$  $+2\log (1-n).$ θ. Þ. 1/0.  $9.872 \times 10^{-4}$ 1013 10.6  $2.37 \times 10^{-1}$ I.1396 Ī·1434 1018 10.9 2.42 9.823 2.48 11.2 Ī·1468 1023 9.775 11.4 2.52 Ī·1490 1028 1033 11.7 2.57 Ī·1521 9.681 12.1 2.65 Ī·1557 9.634 1038 1043 12.4 2.70 ī·1581 9.588

TABLE II.

to the straight line through the second and the seventh. The high values of n for which  $\lambda$  is sensibly constant are noteworthy. The mean value of  $\lambda = 2.90 \times 10^3$ .

In order to obtain some test of the order of accuracy with which the composition of this compound MgCu<sub>2</sub> can be calculated, from points

on a portion of one of the adjacent branches of the liquidus, calculations have been made on the assumption that the composition of the compound may be represented by Mg<sub>2</sub>Cu<sub>5</sub> or by Mg<sub>3</sub>Cu<sub>7</sub>. The results shown in Table III were obtained.

The points for Mg<sub>2</sub>Cu<sub>5</sub> lie on a curve concave to the straight line joining the first and the last. The points for Mg<sub>3</sub>Cu<sub>7</sub> also lie on a curve concave to the straight line joining the first and the last,

TABLE III.

1/θ.	Mg <sub>2</sub> Cu <sub>5</sub> .	Mg <sub>3</sub> Cu <sub>7</sub> .
9·872 × 10 <sup>-4</sup> 9·823 9·775 9·728 9·681 9·634 9·588	2·1622 2·1663 2·1698 2·1723 2·1753 2·1777 2·1797	3·3019 3·3097 3·3166 3·3214 3·3275 3·3333 3·3379

though the average curvature is not as great as that of the previous curve. It appears, therefore, that from an appropriate portion of the liquidus the composition of the compound MgCu<sub>2</sub> can be calculated to an approximation closer than that represented by the hypothetical Mg<sub>3</sub>Cu<sub>7</sub>. The greater the number of points on the portion of the liquidus which have been determined experimentally the closer will be the possible approximation.

It will be noted that these results are confirmatory of the metallographic work of W. R. D. Jones.

If the compound MgCu<sub>2</sub> forms a solid solution, the thermodynamic

equation must contain at least one more term, possibly two more. It seems improbable that results such as the foregoing could be obtained from it. It is to be noted that such solid solutions have been found by Grime and W. Morris-Jones 2 by means of X-ray analysis.

(iii) For the portion of the liquidus from the F.P. of magnesium to the eutectic at 485° C. and for the corresponding portion of the solidus, it will be found that the boundary conditions can be satisfied by assuming that the liquid phase consists of monatomic molecules of copper in monatomic molecules of magnesium. If the constitution of the solid phase is the same, the form of the equation must be:—

$$-\log(I-n) + \log(I-n') = \lambda/R\theta - \lambda/R\theta_0.$$

The solubility of copper in magnesium at a temperature near to 485° C. is 0.03 per cent. according to W. R. D. Jones. This gives  $1.0 \times 10^{-4}$  for the maximum value of n', hence for the calculations involved in the equation,  $\log (1 - n') \geqslant 2 \times 10^{-5}$ . Hence

$$-\log(I - n) = \lambda/R\theta - \lambda/R\theta_0$$

is of the same order of accuracy as that of the data. The results shown in Table IV were obtained:—

θ.	p.	11.	$\log(1-n)$ .	Ι/θ.
920·5 913 903 893 883	2·86 5·89 8·40 10·60	1·11 × 10 <sup>-2</sup> 2·34 3·39 4·34	0·0 <u>1</u> ·9952 <u>1</u> ·9897 <u>1</u> ·9850 <u>1</u> ·9807	10·864 × 10 <sup>-4</sup> 10·950 11·074 11·198 11·325

TABLE IV.

These points lie close to the straight line through the second and the fourth. This is consistent with the simplicity of the constitution of the liquid solution and of the solid solution of copper in magnesium. The mean value of  $\lambda = 1.99 \times 10^3$ .

(iv) For alloys from the concentration of the eutectic at 485° to that corresponding with the compound Mg<sub>2</sub>Cu the liquid solution must give rise to the compound Mg<sub>2</sub>Cu, according to the reaction

$$Cu + 2 Mg = Mg_2Cu$$
.

TABLE V.

θ.	<i>p</i> .	n.	$+\log n$ $+2\log (\mathbf{I}-n).$	1/θ.
773 778 783 788 793 798 803	34·4 35·6 36·8 37·9 39·0 40·2 41·4	1.67 × 10 <sup>-1</sup> 1.74 1.83 1.89 1.96 2.05 2.13	Ī·0641 Ī·0754 Ī·0848 Ī·0948 Ī·1034 Ī·1120 Ī·1201	12·937 × 10 <sup>-4</sup> 12·853 12·771 12·690 12·610 12·531 12·453

<sup>&</sup>lt;sup>2</sup> Grime and Morris-Jones, Phil. Mag., 7, 1113, 1929.

Hence the equation satisfying the boundary conditions must be

$$-\log n - 2\log(1-n) = R/\lambda\theta + \text{const.}$$

The results obtained are shown in Table V. These points lie close to the straight line through the second and the sixth. The mean value of  $\lambda = 5.38 \times 10^3$ .

Again, to get some test of the order of approximation with which the composition of the compound Mg<sub>2</sub>Cu can be calculated by the method

already given, calculations have been made for the hypothetical compound Mg<sub>7</sub>Cu<sub>3</sub>. The results shown in Table VI were obtained. These points lie on a curve concave to the straight line joining the first and the last. argument as to the order of approximation is similar to that given for the case of MgCu<sub>2</sub>.

These and the results preceding show that the composition of the liquid phase is the simplest possible, there being no compound in solution,

TABLE VI.

ı/θ.	Mg₁Cu₃.
12·937 × 10 <sup>-4</sup> 12·853 12·771 12·690 12·610 12·531 12·453	3·1129 3·1426 3·1662 3·1936 3·2152 3·2369 3·2564

as in the cases of the copper and tin alloys and of the copper and zinc alloys. The results do not give any evidence of the existence of a compound MgCu.

# Summary.

- I. The constitution of the liquid solution is the simplest possible, consisting of monatomic molecules of copper and of magnesium.
- 2. The constitution of the solid solution of magnesium in copper and of copper in magnesium is likewise the simplest possible.
- 3. The results are consistent with the existence of the compounds MgČu<sub>2</sub> and Mg<sub>2</sub>Cu as shown by the equilibrium diagram given by W. R. D. Jones.
- 4. Grime and W. Morris-Jones examined this system by X-ray analysis. They found "a region of solid solution extending on both sides of the Cu<sub>2</sub>Mg composition." This is at variance with the results given by W. R. D. Jones.

  5. The results of the foregoing thermodynamic analysis are all in
- agreement with the metallographic work of W. R. D. Jones.

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# THE SWELLING OF PROTEIN FIBRES. PART I THE SWELLING OF COLLAGEN.

By D. JORDAN LLOYD, R. H. MARRIOTT AND W. B. PLEASS.\*

Received 27th January, 1933.

Previous work on the absorption of water by gelatin has suggested that the water in a gelatin jelly exists in two forms: bound water. which may be associated with certain groups in the molecule by coordination or may be localised round ionic centres by electrostatic forces, and free water, which exists in the interstices of the protein framework.<sup>1, 2</sup> The amount of bound water in a protein system probably depends on the number of oxygen or nitrogen-containing groupings, as, for instance, the hydroxyl or amino groups, though the association between water and protein is probably rather a dynamic than a static equilibrium. The amount of free water in a gelatin jelly depends on the concentration of the sol from which the jelly was set, but in all jellies it becomes greatly increased if the jellies are in contact with acid or alkaline solutions resulting in the establishment of a Donnan equilibrium. At present, no satisfactory method has been suggested for measuring the variations in the amount of bound water under varying external conditions, although the amount of free water can be shown to vary within very wide limits. It has been shown, however, that the total amount of water in a gelatin jelly under all external conditions depends to a great extent on the internal arrangement taken up by the protein molecules at the time when the warm sol originally cooled and passed over into the jelly or gel condition.<sup>3</sup> The setting of a gelatin sol to a gelatin jelly has recently been shown by Katz, Derksen and Bon 4 to be associated with a change in the X-ray diffraction diagram, the diagram for the sol indicating an amorphous structure while that for the jelly has the well-defined rings characteristic of crystal structure. Jelly formation is therefore due to the development of some degree of organisation in the system. It seemed, therefore, desirable to study the swelling of a system containing gelatin molecules under conditions where organisation of the structure had preceded as far as possible. Such a system exists ready to hand in the collagen fibres of the skin, connective tissue and tendons. Katz and Gerngross 5 showed some years ago that collagen fibres gave an X-ray diffraction diagram with the definite rings characteristic of crystal structure and that the spacing of these rings suggested that the long protein molecules of the collagen fibres were to be regarded as lying parallel to the long axis of the fibre. The molecules are arranged, therefore, with the minimum amount of space between them and the possibility arises that the cohesive forces

<sup>\*</sup> From the Laboratories of the British Leather Manufacturers' Research Association.

Jordan Lloyd, Biochem. J., 14, 147, 1920.
 Jordan Lloyd and Phillips, Trans. Farad. Soc., 29, 132, 1932.

<sup>&</sup>lt;sup>3</sup> Jordan Lloyd, *Biochem. J.*, **25**, 1580, 1931. <sup>4</sup> Katz, Derksen and Bon, *Rec. Travaux Chim. Pays-Bas.*, **50**, 725, 1931.

<sup>&</sup>lt;sup>5</sup> Katz and Gerngross, Koll. Z., 39, 180, 182, 1926.

of the system may be increased by the formation of cross linkages between adjacent molecules. Collagen fibres arise by the elongation of the fibroblast cells of the primary connective tissue. It is probable that each fibre is the product of a single fibroblast cell. The fibres can be seen to consist of a number of fine fibrils lying closely packed together in parallel order. The fibrils in fresh tissues show undulations and are probably in the form of elongated spirals. Each fibre is bound at intervals with rings of reticular tissue  $^{6,7}$  and in the skin the fibres run several together bound by outer rings of reticular tissue to form the fibre bundles. The fibril, which may be regarded as "collagen" in its natural state, is in an ox-hide about 2 to 5  $\mu$  in width. The gelatin molecule with its side chains may be considered to be the order of 10 to 15 Å in width. The fibril, therefore, is built up of some thousands of gelatin molecules lying side by side. Fibres are about 30  $\mu$  in diameter and are, therefore, built up of about 100 fibrils, while fibre bundles are 75  $\mu$  and upwards and consist therefore of, say, 5 to 10 fibres.

While the fibril is to be regarded as the structural unit of collagen which it would be desirable to compare in its properties with a gelatin jelly, the technical difficulties associated with making quantitative studies on the swelling of single fibrils have so far appeared to be insuperable. Doubtless for this reason references to the swelling of collagen recorded in the literature refer to the behaviour of tissues, such as skin pieces (Kaye and Jordan Lloyd 6 and others), tendons,8 single fibre bundles 9 or "hide-powder." 10 In comparing the swelling of such systems with that of gelatin jellies, it must be borne in mind that water may pass either into or in between the fibrils.<sup>6</sup> The water in a swollen collagen fibre may, therefore, be within the fibril, either as bound water or free water, or between the fibrils as interfibrillary water. The microscopical study of a fresh fibre from skin or tendons suggests that in this state there is little interfibrillary water. naturally occurring collagen fibre contains, however, a considerable amount of water. Recent determinations on the corium of ox-hide show that this tissue contains 67 per cent. of water and 33 per cent. of dry matter which consists almost entirely of collagen. Collagen fibres from this material should therefore be compared in their behaviour to 33 per cent. gelatin jellies, and any striking discrepancies between the two systems should be attributed partly to histological structure and partly to molecular organisation. The work on collagen swelling already quoted shows that the swelling of collagen fibres resembles the swelling of gelatin in many ways, although the degree of swelling under the same external conditions is very much less. In solutions free from salts, swelling is minimal in neutral or nearly neutral solutions and shows a well-defined maximum in acid solutions and a badly defined maximum in alkaline solutions, both maxima being repressed in the presence of salts and both being attributable to the existence of a Donnan equilibrium. Swelling of this type is due to shortening and thickening of the fibrils, which leads to thickening and loss of area in the case of skin pieces. The fibrils become distended and closely adpressed and the obliteration of the internal surfaces of the skin

Kaye and Jordan Lloyd, Proc. Roy. Soc., 96B, 294, 1924.
 Kaye, J. Internat. Soc. Leather Trades Chem., 13, 73, 1929.
 Kuntzel, Koll. Z., 40, 264, 1926.

<sup>9</sup> Marriott, Biochem. J., 26, 46, 1932.

<sup>10</sup> Porter, J. Soc. Leather Trades Chem., 5, 259, 1921.

causes translucency. The  $p_{\rm H}$  range of minimal swelling appeared to be extensive. In solutions of salt which are nearly neutral swelling occurred by a separation of the fibrils so that water flowed in between them, and owing to this development of internal surfaces the skin pieces became chalky white. This type of swelling, due to separation of the fibrils, was also found to occur in fresh skin with dilute acids and alkalies. The work of Kaye and Jordan Lloyd summarised above dealt with skins which had not been freed from non-collagenous proteins; that of Marriott only covered the acid range. It was, therefore, considered useful to extend the experiments over a wider range of experimental conditions on carefully purified material.

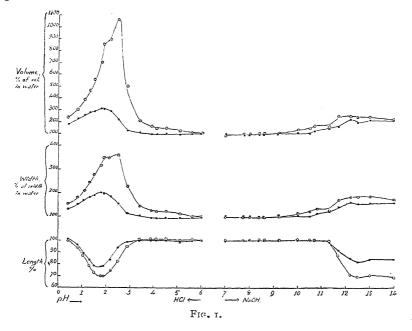
For this purpose collagen from ox-hide was used. In some cases single fibre-bundles were studied; in others, pieces of prepared skin free from non-collagenous proteins. The fibre bundles were teased singly out from pieces of fresh hide and used in the fresh condition. They represent collagen as laid down in the body which has not received any chemical treatment and can be regarded as substantially free from other proteins. Single fibres from the prepared skin were also examined. The isolated single fibres were studied by the method previously described by Marriott, extra precautions being taken to wash out the observation chamber with four changes of solution between each observation so as to ensure that no error occurred in the recorded pr value due to adsorption of hydrogen or hydroxyl ions on the glass walls. The dried collagen was prepared by soaking fresh ox-hide for a week in a 4 per cent. suspension of lime to remove coagulable proteins, mucoids and hair. The lime was removed by treatment with ammonium chloride and the material was submitted for a short time to the action of trypsin which digests any collagen which has been acted on by the lime but does not hydrolyse the unaltered collagen at the temperature used, namely, 370.11 The material was washed free from chlorides, the final washings being carried out with water brought to  $p_{\rm H}$  5 by dissolved carbon dioxide, and dried with acetone. The ash content determined as sulphate was 0.52 per cent. of the collagen dried in the water oven. Assuming that the base is entirely calcium, this would give a calcium content of 0.2 per cent. Drying changes the properties of the fibres, but the convenience of using material which can be stored in bulk is considerable.

Pieces about an inch square were taken for direct weighing experiments. In carrying out such experiments on the dried collagen, there is a considerable variation between duplicated results, caused largely by the influence of the fibre-weave, which varies in different parts of the hide.<sup>6</sup> All weighings were calculated to a percentage on the dry weight after drying at 100°.

Experiments on the action of hydrochloric acid and sodium hydroxide respectively on single collagen fibres are summarised in Fig. I. Each curve is the result of a series of observations on the same fibre. The magnitude of the variations from fibre to fibre are considerable, and results obtained for one fibre must not be directly correlated with those obtained for another. This is largely due to difficulties inherent in the method of holding the fibres. Fresh and dry fibres are compared. Swelling is expressed as a volume change (calculated), increase in width being, over the greater part of the  $p_{\rm H}$  range, accompanied by decrease in

<sup>&</sup>lt;sup>11</sup> Marriott, J. Internat. Soc. Leather Trades Chem., 16, 6, 1932.

length. For fresh fibres, maximum increase in volume is at pH 2.5-2.6 in acid solution and at about  $p_H$  12 with a possible secondary maximum at pH 10.7-11.3 in alkaline solution. For dry fibres, maximum increase in volume is at  $p_{\rm H}$  1.8 in acid solution and at about 12.2 in alkaline solution. Maximum width is at  $p_{\rm H}$  2.5 and about 12.5 for the fresh fibre;  $p_{\rm H}$  I·8 and about I2·2 for the dry. Minimum length is at  $p_{\rm H}$  I·9 and I2·5 for the fresh fibre;  $p_{\rm H}$  1.7 and 12.5 for the dry. It is to be noticed that with fresh fibres maximum volume does not coincide with minimum length in acid solutions (see also Marriott,9); in alkaline solutions the position of the maxima are not well marked and it is difficult to form any definite conclusions. It is also to be noticed that dry fibres swell very much less than fresh and require a higher concentration of reagent for maximum effect. This is similar to the effect of drying on gelatin.3 The most striking feature of the curves is, however, the long



range of  $p_{\rm H}$  over which practically constant dimensions are retained. This seems to be a characteristic of fibres. The stable range extends from  $p_{\rm H}$  5.5-9 for fresh fibres and from  $p_{\rm H}$  4-10 for dry fibres.

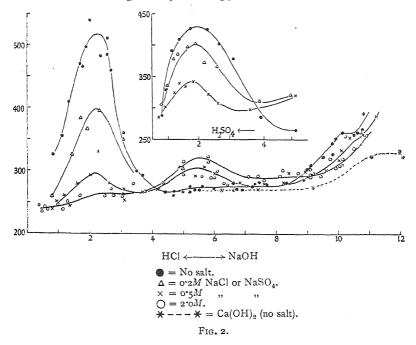
Direct weighing experiments carried out on larger pieces of prepared collagen with the technique previously described for gelatin 12 confirm the general shape of the swelling curve in acid and alkaline solution. This is given in Fig. 3. There is a slight indication of a position of minimum swelling at  $p_{\rm H}$  4.5-4.7 corresponding to that given by Porter for hide-powder. The depression of the curve at this point, however, is of the same order of magnitude as the experimental error and it is felt that a truer impression is gained by regarding the curve as substantially flat between  $p_{\rm H}$  4.5 and 8. The presence of sodium chloride in the hydrochloric acid systems suppresses swelling considerably and

<sup>12</sup> Jordan Lloyd and Pleass, Biochem. J., 21, 1352, 1927.

in the sodium hydroxide systems it suppresses swelling less obviously (see also Kuntzel and Phillips.) Over the stability range of  $p_{\rm H}$  the presence of sodium chloride causes very considerable swelling, which differs, however, in character from acid and alkaline swelling, since it is not associated with contraction of the fibres. When considered at the maximum, solutions of sulphuric acid cause much less swelling than hydroxide acid and calcium hydroxide much less than sodium hydroxide solutions. Repression of swelling by sodium sulphate is shown in the acid range and increase of swelling over the stability range.

Previous work <sup>14</sup> has shown that swelling in acetic and lactic acids is very close to that in hydrochloric acid at the same value of  $p_H$ .

The general similarity in form of the  $p_H$ -swelling curves of collagen fibres and those of gelatin jellies suggests that the same factors are



responsible for swelling in both systems. In the collagen fibres, therefore, charged centres exist in the protein molecule which play the same rôle as in gelatin jellies in setting up a membrane equilibrium and causing an inflow of free water into the system. For the same concentration of protein in fibre and jelly, however, the increase in free water under conditions of acid or alkaline swelling is considerably less. So indeed is the amount of water taken up from pure water or from a solution of sodium chloride (see Table I.).

The figures for the collagen fibres have been read off from Fig. 2. Those for the gelatin gel have been read off from Fig. 3 of the paper by Jordan Lloyd 3 to which reference has already been made. It will be noticed that the latter apply to swelling at 0°. At 18° the figures

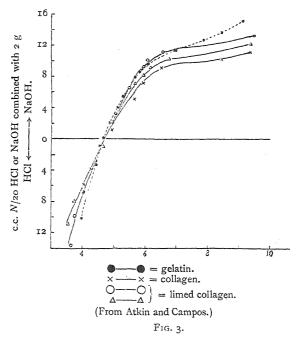
<sup>&</sup>lt;sup>13</sup> Kuntzel and Phillips, *Collegium*, No. 743, 267, 1932. <sup>14</sup> Pleass, *Biochem. J.*, **23**, 358, 1929.

TABLE I.

	Dried Collagen Fibre (33 Per Cent.). $t = 18^{\circ}.$	Dried Gelatin Gel (33 Per Cent.). $t = 0^{\circ}$ .
Water in system in equilibrium with water, per 100 parts of protein	265 — 100 = 165	600 - 100 = 500
Increase of water in system at $p_{\rm H}$ 2·2-2·3, per 100 parts of protein	520 - 265 = 255	2000 - 600 = 1400
Increase of water in system at $\dot{p}_{\rm H}$ 10-10-1 per 100 parts of	- 50	•
protein Increase of water in system at $p_{\rm I}$ and 0.5M NaCl, per 100 parts	360 - 265 = 95	1500 - 600 = 1100
of protein	305 - 265 = 40	1100 - 600 = 500 (0.2 <i>M</i> NaCl)

which would be comparable with those of the collagen are very considerably higher. Part of the difference in the swelling is undoubtedly to be attributed to the effect of the reticular tissue which binds the fibres and fibre bundles. This tissue exists, however, as rings and not as com-

plete membranes round the fibres, so that the latter are free to swell by bulging out in the spaces between the rings. Since the gelatin gel and the collagen fibre contained originally the same concentration of protein (33 per cent.) and since both may be assumed to have the same amino acid constitution, valuable information on the structure of the two proteins may obtained by comparing the titration curves. Fig. 3 shows sections of the titration curves plotted from the figures of Atkin and



Campos. These authors interpret the section of the titration curve between  $p_{\rm H}$  4.7 and 7.5 to the titration of the free carboxyl groups of the protein, an interpretation with which, in view of the very low

<sup>&</sup>lt;sup>15</sup> Atkin and Campos, J. Soc. Leather Trades Chem., 8, 405, 1924.

content of histidine in gelatin, the authors of this paper are in agreement (see also Jordan Lloyd and Pleass). 16 These curves suggest very strongly that collagen as it occurs in the natural state has fewer free carboxyl groups than gelatin. After liming (and the experiments recorded in Table I. were carried out on limed collagen) the differences were not so great. In any case, it is obvious that the difference in the number of groups capable of acting as negatively charged centres (carboxyl groups) in the two proteins is only sufficient to account for comparatively small differences in the extent of swelling in acid and alkaline solutions. If the portions of the titration curves given by Atkin and Campos between  $p_{\rm H}$  7.5 and 9.5 be interpreted as a measure of the back titration of the ammonium ion to the uncharged amino group, then there is again evidence that gelatin contains a greater number of groups capable of acting as positively charged centres (amino groups) than collagen, though again liming reduces the difference which in any case is insufficient to account for the difference in swelling.

Starting with the assumption that gelatin and collagen consist of the same protein, differing only in the orientation of the molecules, we have the possibilities that the cross linkages may be (I) electrovalent forces between positively and negatively charged centres, e.g., salt linkages of the glutaminic acid-arginine type suggested by Speakman and Hirst <sup>17</sup> as occurring in keratin; (2) covalent linkages across the terminal carboxyl and amino groups of the R groups converted by dehydration into peptide linkages as suggested by Astbury and Marwick, 18 or coordinate linkages either between the R groups or directly across the backbones, e.g.,

$$C=O\rightarrow H-N$$
 $C$ 
 $C$ 
 $N-H\leftarrow O=C$ 

If electrovalent links are present, it should be possible to demonstrate their existence by treating the gels and fibres with salt solutions. It has already been suggested 2 that the swelling of gelatin in salt solutions can be explained by an application of Fajan's principle, namely that salts in which the ions are of equal size and valency are associated with less water than salts in which the ions are unequal in size and valency. Gelatin gellies at or near the iso-electric point swell more in salt solutions than in water and this can be explained as the conversion of the gelatingelatin zwitterion salt to a mixed gelatin-electrolyte salt :-

Jordan Lloyd and Pleass, J.S.C.I., 51, 1076, 1932.
 Speakman and Hirst, Nature, 128, 1073, 1931; Trans. Farad. Soc., 29, 148,

<sup>1932.

18</sup> Astbury and Marwick, Nature, 130, 309, 1932. Astbury, Trans. Farad. Soc., 29, 139, 1932.

Collagen fibres also swell in salt solutions and this swelling can be shown microscopically to be due entirely to the separation of the fibrils, a condition well recognised in leather chemistry and described graphically as "opening up" of the fibre. This "opening up" of the fibrils of a fibre also occurs in dilute solutions of acids and alkalies, 9, 19 a proceeding which can also be explained on the same theory. It is of course important to bear in mind that the difference in dimensions between molecules and fibrils is very considerable and the interfibrillary spaces which appear in weak acid and alkali and in salt solutions are of microscopic dimensions. Nevertheless the hypothesis that in the fibril the molecules are so oriented that a number of positive and negative charged centres are localised on the surface and form electrovalent bonds with the oppositely charged centres of adjoining fibrils does not seem an unreasonable extension of the argument. The diffusion of electrolytes into the interfibrillary spaces would provide a new balance of ions and weaken the interfibrillary forces. It is important in this connection to notice that both dry gelatin and collagen swell less in salt solutions than the undried proteins and that it is very difficult to open up the fibres of tropical sun-dried skins so that the constituent fibrils become visible. It is not impossible that the electrovalent salt link postulated as existing between fibril and fibril has been converted by loss of water into a covalent link, possibly of the peptide type. Possible evidence in support of this is found in the fact that treatment with trypsin leads to a certain degree of opening up of sun-dried fibres. The resistance of dried skins and fibres to swelling was originally attributed by Kaye and Jordan Lloyd to the coagulation of interfibrillary proteins. Marriott's later work, however, has shown that a similar phenomenon occurrs when these have been removed and, therefore, the chemistry of the collagen must be involved.

The holding together of the molecules of the collagen fibril, however, cannot be due to links of the electrovalent type. Gelatin is soluble in warm water and in cold, concentrated acid and alkali. Collagen from hide fibres of the ox is completely insoluble under all these conditions but can be made soluble (i.e., transformed into gelatin) by the action of dilute alkali, particularly calcium hydroxide solution in the cold. The reaction proceeds only slowly and is accompanied to a slight extent by a hydrolysis of the molecule or splitting of the peptide links. The main reaction in converting collagen into gelatin, however, is not a hydrolytic splitting of a peptide link and it is suggested that it may be due to the rupture of co-ordinate links between adjacent molecules :--

<sup>19</sup> Kaye and Jordan Lloyd, *Biochem. J.*, **18**, 1043, 1924.

If the change postulated above actually occurs, washing out the alkali would not lead to a reversion since 5-atom rings are very stable structures. (Ruzicka, 20 see also Bennet. 21)

The evidence of the loosening between the fibrils of an electrovalent link of the type shown below, which would have a length of about 13 to 15 Å units:-

N H H N

C C O 
$$^{+}N$$
 N C C

C C C C C C C

H<sub>2</sub> || H<sub>2</sub> H<sub>2</sub>

O NH

(glutamic acid residue) (arginine residue)

about 15 Å

or of a direct co-ordinate link within the fibrils of the type shown above. which would have a length of about 5 Å units should be obtainable by means of X-ray analysis.

While suggesting that the collagen fibre is made up of fibrils each composed of a bundle of protein molecules held together by co-ordination between the backbones and with the charged centres oriented to the outside of the fibril, it is not suggested that all possible charged centres are in this position. It seems certain that both positive and negative charged centres lie within the structure of the fibril. These react with the ions of both acids and alkalies, setting up a Donnan equilibrium inside the substance of each fibril. If the fibrils are held together by co-ordinate links, the inflow of water must lead to distortion with twisting of the fibrils and shortening in length.22 This condition leads to an expansion of the fibrils across their diameter and in the woven skin the adjacent fibrils become closely pressed against each other and this leads to adjacent fibres also becoming closely pressed together and the whole skin becomes turgid and translucent, a condition described in leather chemistry as "plumped."

The collagen fibre of the ox-hide contains, as stated above, about 67 parts of water to 33 parts of protein. The fibre, therefore, must contain channels filled with liquid into which the ions of electrolytes can diffuse. The capillary nature of these spaces and the strong cohesive forces due to co-valent cross linkages, however, act against the inflow of water due to the establishment of a Donnan equilibrium and reduce the swelling of collagen to a very much lower value than that of an equally concentrated gelatin jelly under the same external conditions. The free water in a swollen collagen fibre is, therefore, very much less than the free water in a gelatin jelly of equal protein concentration. The evidence of water-equilibrium suggests also that the water is less—the 33 per cent. gelatin jelly increases its bound water when in contact with water; the collagen fibril does not do so. Whether this is due to the molecular cross-linkages in the latter making it a very stable structure or to

Ruzicka, Helv. Chem. Acta, 9, 499, 1926.
 Bennet, J.S.C.I., 51, 776, 1932.
 Jordan Lloyd, Trans. S.C.I., 51, 141, 1932.

possible centres for co-ordination of water in the molecule being blocked, it is not yet possible to say.

## Summary.

1. The swelling of collagen fibres from ox-hide may be compared to that of a 33 per cent. gelatin jelly. These systems are alike in chemical constitution, but differ in histological structure and in molecular organisation. The presence of rings of reticular tissue round the fibres and the orientation of the molecules within their substance with the existence of inter-molecular cross linkages make the cohesive forces of the fibre much greater than those of the jelly.

2. Collagen fibres resemble gelatin jellies in the following features:—

(a) They show swelling in acid solutions which begins at  $p_{\rm H}$  values less than the iso-electric point of the protein and rises to a well-defined maximum, afterwards decreasing with decreasing  $p_{\rm H}$  value. Hydrochloric and also lactic and acetic acids give rise to swelling of similar order at the same external  $p_{\rm H}$ . Sulphuric acid causes swelling with a lower value at the maximum. The presence of salts represses swelling in acid solutions in accordance with the predictions of the Donnan theory of membrane equilibria.

(b) They show swelling in alkaline solutions which does not, however, begin at  $p_{\rm H}$  values immediately greater than the iso-electric point but first becomes certain at about  $p_{\rm H}$  9·5. There is a suggestion of a swelling maximum at  $p_{\rm H}$  10-10·5, followed by a considerable increase in volume at higher values of  $p_{\rm H}$  which are not true equilibria but are due to the destructive action of the alkali on the fibre-structure. Swelling in sodium hydroxide is considerably greater than in calcium hydroxide at the same  $p_{\rm H}$  value.

The presence of salts represses alkaline swelling.

 $(\bar{c})$  They show swelling in salt solutions at  $p_{\rm H}$  values near the isoelectric point.

(d) If once dried, their power of swelling is considerably reduced except possibly in strongly alkaline solutions.

3. Collagen fibres from ox-hide differ from gelatin jellies in the

following features :-

(a) Under the same external conditions swelling is always less than in a gelatin jelly set at the same concentration of protein (33 per cent.).

(b) There is not a sharp minimum of swelling corresponding to the isoelectric point but a well-marked stability zone from about  $p_{\rm H}$  5.5 to about  $p_{\rm H}$  9, over which fibre width, length and volume remain constant.

(c) Swelling in acid and alkaline solutions is generally accompanied by contraction along the axis of the fibre. The first stages of swelling in these solutions are, however, not accompanied by contraction but show

splitting into fibrils.

(d) Swelling in salt solutions at  $p_H$  values near the iso-electric point,

is due to a splitting of the fibre into its constituent fibrils.

4. It is suggested that the collagen fibril is composed of a bundle of protein molecules arranged with their backbones parallel to the long axis of the fibre and held together by co-ordinate links between the backbones of adjacent molecules; the R groups terminating in charged centres  $(-NH_3^+ \text{ or } - \text{COO}^-)$  being arranged so that some are situated within the fibril but a large number are brought on to its outer surface. It is further suggested that in each fibre the fibrils are held together by electrovalent forces between positive  $(-NH_3^+)$  and negative  $(\text{COO}^-)$  charged centres on their outer surfaces besides being mechanically bound by the reticular tissue.

The authors wish to acknowledge with thanks the permission of the Council of the British Leather Manufacturers' Research Association to publish this work.

# STUDIES ON ADSORPTION. PART III. THE EFFECT OF ACTIVATION OF THE CHARCOAL ON THE ISOTHERMALS OF CARBON TETRACHLORIDE.

By L. J. Burrage.

Received 30th Fanuary, 1933.

In order to examine from a practical standpoint the views expressed in Part I of this series, it was decided to determine the  $\mathrm{CCl_4}$  isothermals of a number of charcoals in different stages of activation and so be able to tabulate them in their activation order. In this way an insight would be gained as to the best method of activation and the best starting material. Twenty-five different charcoals were employed, embracing a number of methods of activation and starting materials.

# Experimental.

A full description of many of the charcoals employed has been given previously and the references are contained in Table I. In the case of new charcoals the apparent densities are given in this table, the starting materials and methods of activation being given later in the text.

TABLE I.

Charcoal.	Reference.	Charcoal.	Reference.
A B C D I E I F I G K I L I M I M 2 M 3	J. Physic. Chem., 32, 441, 1928.  """  Proc. Roy. Soc., 130, 610, 1931.  Apparent Density 0·349  J.S.C.I., 47, 372T, 1928  Apparent Density 0·311  J. Physic. Chem., 34, 2202, 1930.  Apparent Density 0·445  J. Physic. Chem., 34, 2202, 1930.	M (B) N N 1 P Q R	J. Physic. Chem., 34, 2202, 1930. Apparent Density 0.404  ,,,,,0.392 ,,,,0.427 ,,,0.60  Proc. Roy. Soc., 132, 460, 1931. Apparent Density 0.416 ,,,,0.294 ,,,,0.294 ,,,,0.379 ,,,,0.250 ,,,,,0.38

The isothermals, which were carried out at 25° C., consisted of a desorption series from an initial point of 70 mm., and finally resorption to saturation. Seven points were obtained on each isothermal covering the range from II5 mm. to 0.01 mm. The method employed was that of desorbing to constant pressure in an air stream. (Methods 2A and B). The results of these determinations are shown in Figs. I-4, the charcoals being grouped in the various diagrams in the order shown in Table II. In each case between I and 4 gms. of 10-12 mesh charcoal were taken

<sup>&</sup>lt;sup>1</sup> Burrage, Chem. News., 145, 206, 1932.

for the experiment, the apparatus employed being that used in the determination of isothermals by the retentivity technique.<sup>2</sup>

TABLE II.

Figure.	Charcoal.	Method of Activation.	Starting Material.
I	G	Steam	Palm Nut Shell
	Мı	**	,,
	M 2	**	,,
	M 3	,,,	"
	M 4	,,	,,
	M 5	,,	,,
	M 6	"	,,
2	С	,,	Coconut Shell
	Dг	,,	,,
	Fı	"	,,
	M (B)	,,	
	M (A) N	7,01	Brazil Nut Shell
		ZnCl <sub>2</sub>	Almond Shell
	Nı	,,	**
3	K 1 P Q R T E 1	$P_2O_5$	Peat
-	P	ZnCl <sub>2</sub>	,,
	Q		,,
1	R	Steam	,,
	$\underline{\underline{\mathbf{T}}}$	$ZnCl_2$	_,,,
	EI	Steam	Coal
4	A	Air	Birchwood
.	В	$ZnCl_2$	Pinewood
1	A B L L I S	Steam	Beechwood
)	Lı	,,	,,
1	S	Air	,,

#### Discussion.

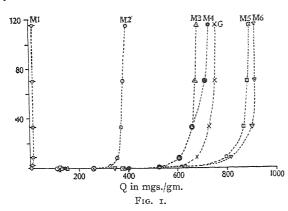
The series M I-M 6 (Fig. 1) made from palm nut shell represents stages of increasing activation, M I being the unactivated charcoal. It will be seen that the saturation value increases steadily with the degree of activation, whereas the values at 0.01 mm. pass through a maximum at M 3. As regards this region M 2 is underactivated, M 4 and G slightly over-activated, and M 5 and M 6 still more so, there being a maximum quantity adsorbable with the optimum degree of activation. The theoretical reasons for this have already been discussed. Charcoal G, which has been added to this diagram, is made from the same starting material and is intermediate between M 4 and M 5 as regards the degree of activation.

Fig. 2 represents the isothermals of the other nut shell charcoals. D I, M (B) and F I are underactivated, while C corresponds closely to the optimum value. Of the remainder M (A) is underactivated, while N and N I are distinctly overactivated. The two latter are made from a somewhat soft nut shell and hence would be readily attacked by activating

Allmand and Burrage, J.S.C.I., 47, 372T, 1928; Burrage, J. Physic. Chem.,
 34, 2202, 1930.
 Part I of this Series, Trans. Far. Soc., 29, 445, 1933.

agents giving rise to a charcoal which is overactivated. In Fig. 3 are given the peat and coal charcoals. The only example of the latter, E I, is difficult to place in its activation order, as at high pressures it corresponds to a fairly well activated charcoal, while at low pressures it is underactivated. An alternative view is that it is much overactivated

p in mm.



at both high and low pressures. This latter view may well be the since case, was the starting material. The peat charcoals R, K I. P and O are all over - activated, while T represents the most advanced stage of activation of any charcoal in the series.

In Fig. 4 are shown the softwood charcoals, S

and A being under-activated, B highly activated and L and L I corresponding closely to the optimum degree of activation at low pressures.

From these data it would appear that the best charcoal for adsorption at low pressures can be made from nut shell, activated by steam, whereas for high pressures the best starting material is peat, activated by chemical means. The chemically activated charcoals, however,

p in mm.

possess inorganic material which would poison some of the active centres, thereby lowering the efficiency at low pressures; but solely this not is responsible for position, since charcoals N and N I have less than I per cent. of inorganic material and yet retain little CCl4 in this region.

The chief data from these graphs have been plotted in Fig. 5—the quantity of vapour ad120 MB FI C NI N

80 40 40 600 800 1000

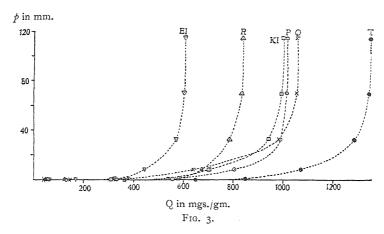
Q in mgs./gm.

FIG. 2.

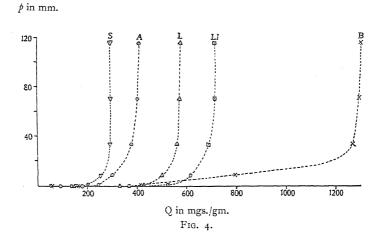
sorbed at saturation—and in Fig. 6—the quantity adsorbed at 0.01 mm. Since it has been shown 4 that CCl<sub>4</sub> is only adsorbed at active centres it follows that these graphs give the relative order of activation of the charcoals at high and low pressures respectively. In Fig. 5 the saturation quantities are plotted against the apparent densities. If

<sup>&</sup>lt;sup>4</sup> Part II of this Series, Trans. Far. Soc., 29, 458, 1933.

a series of charcoals be considered whose unactivated materials have approximately the same apparent density, e.g., palm nut shell and coco-nut shell, they are found to lie very close to a straight line. All the available data have been plotted on this graph, but they do not all lie on the same line since the apparent densities of some of the

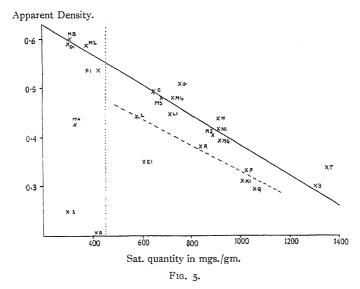


unactivated materials may be much less than others. If the apparent density of the unactivated material is very low it will alter but slightly with activation, giving a line more parallel to the quantity axis than is the case with dense starting materials. This is indicated by the dotted line through the peat charcoals. These are all briquetted and therefore

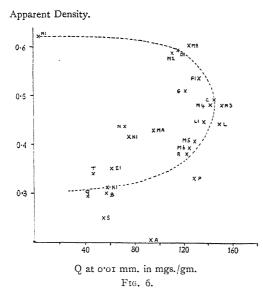


the apparent density depends on the degree of compression as well as on that of activation; hence it may well be that T is obtained by a denser briquetting than are the other peat charcoals. From this graph it would appear that at high pressures the quantity adsorbed is quite independent of the starting material, thus depending entirely on the degree of activation.

In Fig. 6 the quantities of CCl<sub>4</sub> adsorbed at 0.01 mm. are plotted against the apparent density, as in the previous case. Considering the



same group as before it is seen that the curve passes through a maximum, showing that there is an optimum degree of activation at low pressures. It is clear that under the best conditions this cannot exceed 160 mgs./gm.



The same remarks apply to those points which do not fall on this curve as in the previous case.

That this maximum would probably has been suggested on theoretical purely grounds.3 From foregoing results it would appear that, in order to make a charcoal which has a high capacity at either high or low pressures, it is not important as to the starting material or the method of activation. The resultcharcoal depends entirely on the degree to which the activation can Steam is be controlled. a mild oxidising agent

and nut shell, a substance fairly resistant to attack, therefore the degree of activation can be easily controlled, but in the case of chemical activation of a softer material, the action is too drastic and a high stage of activation is brought about, involving a large capacity at high, but only a small capacity at low pressures. The concentration of the chemical reagent and the time and temperature are factors which must be carefully controlled in order to produce a charcoal which has high capacity at low pressures. Some form of extraction would also be necessary to remove inorganic material from the active centres if the optimum degree of activation were to be achieved by this method.

One other point of interest has arisen from this work in connection with drift. Charcoals A and S were known to exhibit drifting properties

to a very considerable extent, but this was also found with certain other charcoals when charging at 70 mm. (Table III).

Reference to Fig. 5 shows that all these charcoals lie on the same side of the dotted line, hence it would appear that the effect of drift is most

Quantity in mgs./gm. Charcoal. Initial. Final. Мі 12.4 Dг 277.6 297.2 M (B) 263.4 303.9 M (A) 310.7 325.3 M 2 337.4 369.9 408·I 420.7

TABLE III.

prominent in underactivated charcoals. A possible mechanism for this has already been advanced, anamely that, in underactivated charcoals the activation pores are filled with a  $C_x O_y$  sponge, but the pores are very fine, hence it is much more difficult for the  $C_x O_y$  to be dislodged by the  $CCl_4$  molecules from these pores than from the larger ones of the more highly activated charcoals.

#### Summary.

The CCl $_4$  isothermals of 25 charcoals, in differing states of activation and made from different starting materials, have been determined at 25° C.

The charcoals have been arranged in their order of activation and the effect of increasing activation of the low pressure portion of the isothermal discussed.

A detailed examination of the different methods of activation and the effect of different starting materials on the final isothermal has been made.

An explanation has been advanced for the drift observed in certain cases in the determination of  $CCl_4$  isothermals.

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#### STUDIES ON ADSORPTION. PART IV. OF THE ACTIVATION CHAR-EFFECT OF COAL ON THE ISOTHERMALS OF WATER, AND ITS RELATION TO HYSTERESIS.

By L. J. Burrage.

# Received 13th February, 1933.

In order to examine the effect of activation of the charcoal on the water isothermal, and its relation to hysteresis, a series of experiments has been carried out, similar to that for CCl4 in a previous publication.1 The same twenty-five charcoals have been employed, and the general technique was that of saturating and desorbing to constant pressure in an air stream.<sup>2</sup> Each experiment consisted of a sorption isothermal up to 17.5 mm., followed by desorption to zero pressure. The saturation point was then determined and two or three desorption points obtained until the original desorption curve was reached, some eighteen points being obtained for each charcoal. The drop from the 17.5 mm. figure to the final desorption curve was usually almost vertical, and those points inside the hysteresis loop have been omitted to avoid an unnecessary complication of the diagrams. In order to ensure that the drift, which is very noticeable in water isothermals, should be eliminated as far as possible in this series, the charged charcoal was allowed to stand at 25° for about a month between each successive point, the complete investigation being carried out over a period of several years. For this reason it is considered that the isothermals in this work must be nearer the true values than those of previous investigations.

Abundant evidence has been obtained of the discontinuous nature of the isothermals, in many instances two different pressure readings being obtained which corresponded to practically the same quantity figure. This point was not under investigation, however, as a large amount of data on this subject had already been obtained 3 by employing the modified retentivity technique, and a much greater number of experimental points would have been necessary to determine the exact structure of the isothermals. The charcoals have been grouped in the diagrams in the same manner as in Part III. of this series. In this latter paper it had been found possible to arrange the charcoals in their order of increasing activation, and it will be seen in the present communication (Table I.) that this order is practically the same as for the water values at saturation. There is a difference, however, from the CCl, values, in that the effect of activation does not cause the saturation value to increase as rapidly as with CCl4. Also CCl4 can only be adsorbed at active centres, whereas water can be sorbed at any point on the surface or by the  $C_XO_Y$ .

<sup>&</sup>lt;sup>1</sup> Part III. of this Series.

<sup>&</sup>lt;sup>2</sup> Methods 1a and b, Chem. News, 145, 206, 1932.

<sup>3</sup> Unpublished work.

<sup>4</sup> Part II. of this Series.

TABLE I.

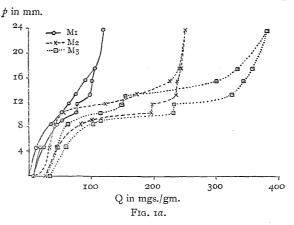
Charcoal.		n Values in /gm.	Charcoal.	Saturation Values in mgs./gm.	
	CCl4.	H <sub>2</sub> O.		CCI4.	H <sub>2</sub> O.
MI S DI M(B) M(A) M2 A FI L EI C M3	13 295 301 307 326 377 411 424 578 607 647 682	119 248 235 239 249 250 238 252 307 319 383 381	L1 M4 G R M5 N N1 M6 K1 P Q B T	715 729 756 842 892 912 912 920 1006 1021 1056 1302 1346	412 386 382 429 398 544 556 439 488 486 574 680 493

#### Discussion.

Considering Figs. 1a and b, which represent a series of charcoals with increasing degree of activation, it is seen that the quantity value at saturation rises continuously as the degree of activation increases. This has already been noted in Table I., but if the values at 4.6 mm. or zero pressure be compared, it will be seen that they increase up to a point and then decrease with increasing activation, in similar fashion to CCl4.

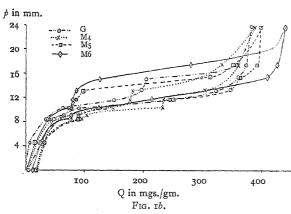
at 0.01 mm.1 In general, this will be p in mm. hold found to throughout the series, showing that the water isothermal is dependent for its position on the degree of activation of the charcoal, as was the case for CCl<sub>4</sub>.

Regarding the hysteresis loop in each case, it is obvious that there is a continual increase on the quantity axis



with increase of activation, the depth of the loop on the pressure axis increasing much more slowly. Although it is somewhat difficult to compare the isothermals at any point, owing to their discontinuous nature, there are very definite indications that the pressure at which the isothermal turns over increases with increase of activation. Fig. 2b shows that M (A), an underactivated charcoal, sweeps over at a lower pressure than N and NI, which are highly activated. With the exception of P, all the charcoals in Figs. 3a and b sweep over at a high

pressure value, which is in agreement with their being highly activated. The same conclusion can be drawn from Figs. 4a and b, which shows, for example, charcoal B, which is highly activated, sweeping over at a much higher pressure than charcoal A, which is underactivated. Of the 25 isothermals studied, the only exceptions to this hypothesis would



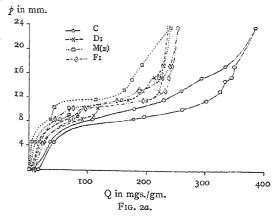
appear to be charcoals C and P.

It is quite clear that the morphological structure of the original starting material, although it persists in the charcoals. exerts little or no influence on the shape of the isothermal the hysteresis loop. This shows quite definitely that the quantity of water adsorbed, although

giving rise to a very different type of isothermal, depends almost entirely on the degree of activation of the charcoal in the same manner as CCl<sub>4</sub>.

That exceptions should appear to the suggestion that the degree of activation is responsible for the pressure at which the isothermal sweeps over is not surprising, if the case is examined in more detail. It has been postulated  $^5$  that the  $C_XO_Y$  exists on the charcoal surface as a sponge which partially fills

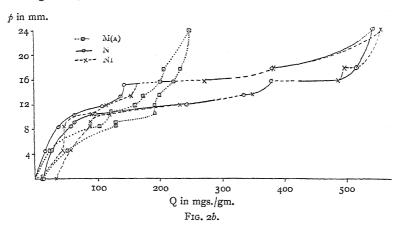
the activation pores. p in mm. If a water isothermal is carried out on a surface such as this. water will be adsorbed by the sponge condensation (and, therefore, the sweep-over) will occur at a lower pressure than if the pores were quite clean. When the  $C_XO_Y$  is completely removed. however, the sweepover will occur at a higher pressure, and



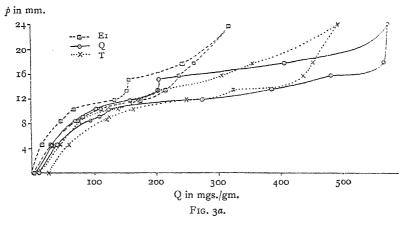
the quantity of water condensed in the clean pores will be greater than that in the same pores with  $C_XO_Y$  present. Therefore, if the charcoal retains the  $C_XO_Y$  very firmly the isothermal will sweep over at too low a pressure. At saturation, however, it may be that the clean charcoal will now adsorb less than when the pores were half filled with  $C_XO_Y$ ,

since some of the clean pores are now too large for liquid to condense in them. On the other hand, the pores at lower pressures are now free from  $C_{\mathbf{X}}O_{\mathbf{Y}}$ , and hence will take up more water, when condensation takes place. The value at saturation on a perfectly clean charcoal will be the resultant of these two opposing effects.

In general, the pressure at which the desorption isothermals sweep



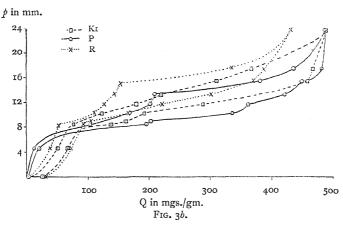
over is 10-12 mm., which is approximately 0.5 relative pressure. It is of interest that previous work, 6 with water on silica gel at higher temperatures, shows the major hysteresis effect to occur at approximately 0.5 relative pressure. In all cases the rate at which equilibrium is attained is definitely longer than with  $\text{CCl}_4$ , but it has been noticed that the underactivated charcoals take very much longer than the others.



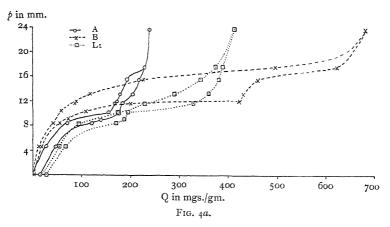
This is similar to the drift observed in the case of the same charcoals with  $CCl_4$ . At a pressure of 15.5 mm. of water vapour drift was observed in all cases. This is probably due to water vapour tending to break up the  $C_XO_Y$  at this pressure, thus cleaning the surface. One must differentiate between drift and hysteresis, although the latter is often used to

<sup>&</sup>lt;sup>6</sup> Lambert and Foster, Proc. Roy. Soc., 134, 246, 1931.

include the former. Drift may either be in the direction of an increasing quantity at a definite pressure, or it may be in the opposite direction, the former, however, being the more usual case. Both of these result from a cleaning of the surface by the removal of  $C_XO_Y$ . Hysteresis is a definite phenomenon, which is quite distinct from drift, although the cleaning up of the surface has a considerable effect on the hysteresis loop.



It has been shown in the present work that the pores which cause the sweep-over in water isothermals are brought about by the activation process, and are not morphological pores present in the original structure. Comparatively little hysteresis is observed at low and high pressures, and this is considered to be due partly to drift and partly to the rectangular form of the isothermal. If one charges at a definite pressure of

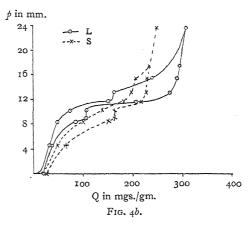


water vapour, which happens to be the pressure at which a step occurs, the quantity will correspond to that of the lowest value, since there would be no force to cause the quantity figure to pass along the horizontal portion of the step. If, however, one now charges to a slightly

higher pressure and then desorbs to the original pressure, the quantity will correspond to the greatest quantity value of the step, and the isothermal will thus exhibit a slight hysteresis.

The central portion of the isothermal shows marked hysteresis which is not of this type. Coolidge has suggested that water is sorbed at low pressures as single molecules and at higher pressures is associated like ordinary water. In the light of recent work the author is in a position to suggest a more detailed mechanism. It has been shown 4 that water

is adsorbed at any point on the charcoal surface or by p in mm. the  $C_XO_Y$  sponge which covers the charcoal proper and largely fills the activation pores. Adsorption will take place at lower pressures as single molecules, but as the pressure is increased there will be a greater tendency for water to be adsorbed as the associated molecule. When that stage is reached, each sorbed water molecule becomes a potential active centre, in that it can condense on itself several other water molecules to



form the associated body. In this way a film can form on the  $\mathsf{C}_X\mathsf{O}_Y$  which partly fills a pore in the charcoal, preventing access to the interior. As the pressure is increased it may pass a point at which condensation should occur in that particular pore, but is unable to do so owing to the surface film. A considerably higher pressure is needed before the film ruptures and condensation takes place. Hence for a given quantity adsorbed the pressure is too high. In desorption, on the other hand, the surface tension forces of the liquid in a narrow capillary would pre-

	C:	harcoal.		Temperature of Evacuation.	Density of Charcoal.
Α.			•	270° 800°	1·880 1·715
С.	٠		•	270° 800°	1·797 1·636
NaOH	and	HCL	Extd.	Soo°	1.618

vent water evaporating from the pore, until pressure outside had been lowered below the original equilibrium pressure at which condensation occurred. Thus, on desorption, for a given quantity,

the pressure is too low. Therefore, the pressure is too great on the sorption curve and too low on the desorption curve, thus giving rise to the observed hysteresis. It is not considered that the effect on the desorption curve is nearly so great as in sorption, therefore one would expect the desorption isothermal to be nearer the correct values. Water has been found to be a comparatively feeble agent for breaking up the  $C_XO_X$ , but this is not surprising, since it is adsorbed by the complex forming a protective layer against bombardment by other water molecules.

That this  $C_XO_Y$  is gradually removed by evacuation, allowing water to enter the charcoal more freely, is shown by Hand and Shiels in their determination of the density of charcoal.<sup>8</sup>

The higher the temperature of evacuation the more  $C_XO_Y$  is removed, thereby allowing water to flow into the charcoal more readily during the density determination, the density of the charcoal becoming less under these circumstances. Extraction also assists in the removal of the  $C_XO_Y$ .

# Summary.

The water isothermals of 25 charcoals in different stages of activation have been determined at 25° C.

The influence of activation on the shape of the resulting isothermals has been noted and discussed.

The effect of activation on the hysteresis loop has been noted and a mechanism suggested.

The influence of  $C_X O_Y$  on the water isothermals and hysteresis loop has been discussed.

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8 J. Physic. Chem., 32, 441, 1928.

# THE DEHYDRATION OF COPPER SULPHATE TRIHYDRATE.

By M. M. Cooper, J. Colvin, and J. Hume.

Received 31st Fanuary, 1933.

In a previous paper 1 were described the results of an investigation of the kinetics of the reaction  $CuSO_4$ .  $5H_2O \rightarrow CuSO_4$ .  $H_2O + 4H_2O$ which led to the view that the reaction occurred in two stages,  $\text{CuSO}_4: 5\text{H}_2\text{O} \xrightarrow{-2\text{H}_2\text{O}} \text{CuSO}_4: 3\text{H}_2\text{O} \xrightarrow{-2\text{H}_2\text{O}} \text{CuSO}_4: \text{H}_2\text{O}.$ vacua, at the temperature of the experiments, the trihydrate is decomposed in the moment of its formation. It appeared, however, that copper sulphate trihydrate in crystalline particles would possess a much lower rate of dehydration than pentahydrate under corresponding conditions. In the hope that further information about the kinetics and energetics of dehydration might be gained, the investigation described in this paper was undertaken. Additional interest attaches to this object in view of Kassel's suggestion 2 that the high energy of activation in certain reactions can be explained by the assumption of the formation of intermediate compounds not apparent in the stoichiometric equation representing the change. The choice of the copper sulphate hydrates is particularly advantageous, since a large amount of information regarding the dehydration of the pentahydrate is

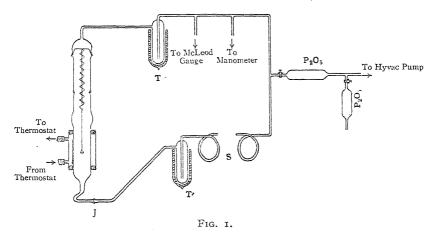
Hume and Colvin, Proc. Roy. Soc., 132A, 548, 1931.
 Kassel, J. Amer. Chem. Soc., 51, 1136, 1929.

available from the work of Garner and Tanner,4 Kohlschütter and Nitschmann 5 and Topley and his co-workers.6

# Experimental.

The preparation of copper sulphate trihydrate crystals of suitable size is a matter of some difficulty. Most of the methods given in the literature involve the dehydration of the pentahydrate and hence yield a product in a very finely divided state, which is useless for the proposed type of experiment. It is essential to have crystals of at least 0.002 mm. in length and in breadth. The only method which gave a satisfactory sample was based on the work of Lobry de Bruyn 7 and was as follows:-

To 100 c.c. of a freshly prepared saturated solution of copper sulphate pentahydrate in methyl alcohol was added about 0.4 c.c. of water and



the mixture was kept in ice over night. The sky-blue crystals which separated were washed with methyl alcohol and dried with filter-paper.

Crystals so prepared were found to be mixed with a small quantity of pentahydrate formed by combination with the water left on the evaporation of the last traces of wet methyl alcohol. This small trace of pentahydrate was decomposed by keeping the sample over fused calcium chloride at 25° for thirty days. Under such conditions no decomposition of trihydrate took place.8 After preparation the sample was stored in a desiccator over a mixture of copper sulphate trihydrate and monohydrate. The crystals selected for use, which appeared to be irregular thick rods of rectangular cross-section, were graded by means of silk with apertures of suitable size, and were measured with a micrometer microscope.

The experimental procedure was similar to that adopted previously

<sup>Partington, J. Chem. Soc., 99, 466, 1911.
Garner and Tanner, J. Chem. Soc., 47, 1930.
Kohlschütter and Nitschmann, Z. physikal. Chem., Bodenstein Festband,</sup> 

<sup>494, 1931.

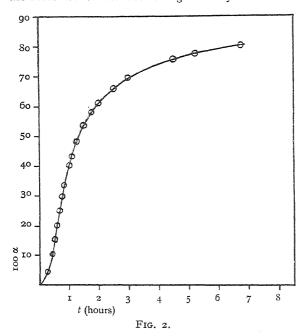
&</sup>lt;sup>6</sup> Smith and Topley, *Proc. Roy. Soc.*, **134A**, 224, 1931. <sup>7</sup> Lobry de Bruyn, Rec. Trav. Chim., 11, 113, 1892. <sup>8</sup> Guareschi, J. Chem. Soc., iiA, 774, 1915.

in the dehydration of potassium hydrogen oxalate hemihydrate. The final form of the apparatus is shown in Fig. 1.

The apparatus was evacuated by means of a Hyvac pump, the water vapour liberated by the reaction being removed by the liquid air traps T, T'. The tubes connecting the balance case and the reaction chamber to the liquid air traps were of I cm. bore tubing. The spiral S of eight turns permitted the breaking of the ground glass junction J and the removal of the reaction chamber.

#### Results and Discussion.

The percentage decomposition-time curves, representing the results, obtained over the temperature range investigated, are similar in form, the most notable features being the very short induction period, indicat-



ing a high rate of nucleus formation. and the extremely slow rate of reacti which ensues at approximately 80 per cent. decomposition. This high nucleus rate of formation is great importance, in that it may be assumed that the entire surface the crystals rapidly becomes covered with a layer of the monohydrate, so that the subsequent course of the reaction might be expected to accord with that predicted by consideration of a contracting envelope. This type

of treatment has already been successfully employed by Topley and Hume  $^{10}$  in the decomposition of calcium carbonate hexahydrate and by Hume and Colvin  $^{1}$  in the dehydration of copper sulphate pentahydrate. The decomposition curve shown in Fig. 2, in which percentage decomposition (100 $\alpha$ ) is plotted against the time, is typical of the whole series of measurements.

The values of the percentage decomposition have been calculated from the changes in the extension of the spring, making the assumption that 100 per cent. decomposition corresponds to the complete conversion of the trihydrate to monohydrate. That no serious error is introduced by the loss of water from the monohydrate at these temperatures has been established by the experiments of Garner and Tanner.<sup>4</sup>

Hume and Colvin, Proc. Roy. Soc., 125A, 635, 1929.
 Topley and Hume, Proc. Roy. Soc., 120A, 211, 1928.

The derivation of the energy of activation depends on the possibility of a rigid comparison of the reaction rates at different temperatures. This may be accomplished in two ways, firstly by determining the rate of loss of water per unit area of interface, or secondly by deriving the rate of advance of the interface through the crystal (the rate of propagation). Clearly these two methods are not independent; but as circumstances dictate, the results may be more amenable to one or other of the modes of treatment.

The former method is that used in the study of the dehydration of copper sulphate pentahydrate by Smith and Topley,  $^6$  who found that the rate (-dm/dt) per unit area of interface steadily diminished as the reaction proceeded, owing to the so-called impedance effect. Hence to effect strict comparison of the rates at different temperatures, it was necessary to extrapolate the curves to zero decomposition. In the case of copper sulphate trihydrate, the great uncertainty introduced by this extrapolation is obvious, since the early observations are influenced by the induction period. For this reason the second method was preferred.

# Derivation of the Rate of Propagation.

For simplicity it is assumed that the crystals may be regarded as rectangular parallelepipeds of square major faces of length l, and thickness  $\theta$ . If the rate of propagation is u, then the fraction decomposed  $(\alpha)$  at time t from the start is

$$\frac{l^2\theta-(l-\mathit{2ut})^2(\theta-\mathit{2ut})}{l^2\theta}.$$

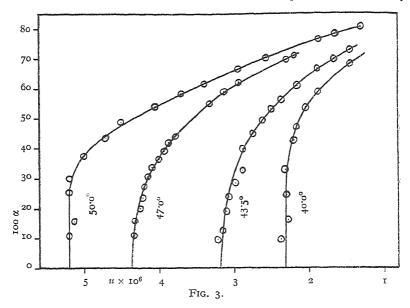
Inserting the dimensions of the crystals (l = .0051 mm. .  $\theta$  = .0015 mm.) this becomes

$$\alpha = \frac{0.048293ut - 0.0469(ut)^2 + 8(ut)^3}{0.073919}.$$
 (1)

TABLE I.

t <sub>obs</sub> .	$t_{\text{obs.}} - \Delta t$ .	$100\alpha = per cent. D.$	u × 106 mm./min.
0 25 30 35 40 45 50 55 60 65 75	10 15 20 25 30 35 40 45 50 60	0.0 = per cent. <i>B</i> .  0.0 10.74 15.63 20.39 25.14 29.96 33.47 37.47 40.42 43.39 48.56	5·20 5·13 5·10 5·20 5·20 5·20 5·00 4·82 4·70 4·50
90 105 120 150 180 270 315 405 570	75 90 105 135 165 255 315 390 555	53.87 58.21 61.16 66.19 69.90 75.77 77.56 80.19 81.96	4.05 3.71 3.39 2.95 2.57 1.86 1.64 1.30 0.96

In deriving this expression the assumptions have been made that the crystals are of uniform size and that nucleation occurs simultaneously over the entire surface. That this latter assumption is not strictly



true is shown by the induction period; so that some uncertainty exists as to the true zero time of the reaction. That is to say, the values of t to be used in equation I will differ from the observational times by

TABLE II.

Run No.	Temperature.	u × 106 mms./min.	Mean 4 . 106 mms./min.
1	40°	2·32	2.41
2	40°	2·51	
3	40°	2·31	
4	40°	2·48	
1	43·5°	3·19	3,53
2	43·5°	3·28	
3	43·5°	3·21	
1	47·0°	4·36	4:35
2	47·0°	3·92	
3	47·0°	4·76	
1	50·0°	5·14	5.19
2	50·0°	5·13	
3	50·0°	5·20	

the same amount as the observational zero differs from the true zero. The magnitude of this correction can be determined in the following way. substituting  $_{\rm By}$ suitable values for ut in equation I, a curve is constructed giving values of α. Then by taking points on this curve and on the experimental decomposition curves at the same tional decomposi-

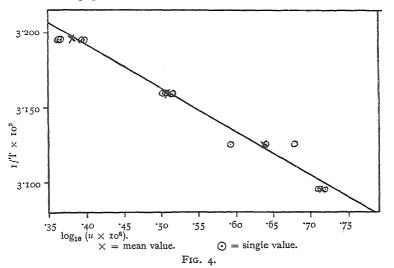
tion, the values of ut can be plotted against the observational times  $(t_{\text{obs.}})$ . But if  $t=t_{\text{obs.}}-\Delta t$  and u, the rate of propagation is a

constant, then  $\frac{ut}{t_{\rm obs.}-\Delta t}=u$ . Clearly the graph  $(ut,\,t_{\rm obs.})$  should be a straight line whose intercept on the time axis gives the value of the correction and hence values of u. When this method is applied to the experimental data, it is found that the lines  $(ut,\,t_{\rm obs.})$ , whilst permitting extrapolation for  $\Delta t$ , show a pronounced curvature, indicating a steadily diminishing value of u. The values of u so obtained are given for the run shown graphically in Fig. 2.

Thus it is necessary to find the values of u at zero decomposition  $(u_0)$  in order that the impedance effect may be eliminated. Fortunately the form of the curve (u, per cent. D) permits of accurate extrapolation, as will be seen from the examples in Fig. 3. Table II. contains the values of  $u_0$  obtained in this way.

# Correction for Self-Cooling.

The extent of self-cooling of the reactant due to the endothermic reaction *in vacuo*, calculated by the method of Smith and Topley, using the data of Carpenter and Jette <sup>11</sup> for the heat of reaction, was found to be negligible at all the temperatures considered.



### The Energy of Activation.

Using the data contained in Table II., the energy of activation may be calculated from the expression:

$$\frac{d \log u}{dT} = \frac{E}{RT^2}, \quad i.e. \ d \log u/d(I/T) = E/R.$$

The curve obtained by plotting  $\log u_0$  against I/T (Fig. 4) is a reasonable approximation to a straight line. From the slope of this line the energy of activation for the reaction

$$CuSO_4$$
.  $3H_2O \rightarrow CuSO_4$ .  $H_2O + 2H_2O$ 

is 15,600 calories.

<sup>&</sup>lt;sup>11</sup> Carpenter and Jette, J. Amer. Chem. Soc., 45, 578, 1923.

#### General Discussion.

As has been seen in the preceding section the values of u obtained by the application of the contracting parallelepiped formula, are not constant, but diminish as dehydration proceeds. Now, in a study of the dehydration of copper sulphate pentahydrate Hume and Colvin. using small crystals, found no decrease in rate u before 80 per cent. decomposition, whilst Garner and Tanner and Smith and Topley, using large single crystals, observed progressive retardation throughout the experiment. These results suggest that the factor which results in the diminishing rate becomes of greater significance as the thickness of the monohydrate shell increases, and thus, though negligible in Hume and Colvin's results, is appreciable in Smith and Topley's, because of the much greater thicknesses involved.

Examination of Fig. 3, in which u is plotted against percentage decomposition, shows that the effects of impedance in the later stages of decomposition become greater at the higher temperatures. This is shown in Table III.

Per cent. D.	u/u <sub>0</sub> at 40°.	u/u <sub>0</sub> at 43.5°.	u/u <sub>0</sub> at 47°.	$u/u_0$ at 50°.
0 20 40 50 60	1.000 0.996 0.957 0.892 0.776	1.000 0.981 0.904 0.826 0.708	1.000 0.981 0.897 0.810 0.697	1·000 1·000 0·938 0·838

TABLE III.

A high value of the ratio  $u/u_0$  indicates that the effects of impedance are slight. It is to be emphasised that the values of u obtained by the method used, for times later than the start, can be regarded as of real significance, only so long as constancy is maintained. The velocity  $u_t$  obtained at time t is clearly the mean velocity that, operating from o to t, would result in the observed decomposition.

Considering the process occurring at the interface, the liberation of water molecules must result in the existence there of some pressure of water vapour, virtually a constant pressure if the rate of escape of water through the lower hydrate is great. Then the constant pressure will be accompanied by a constant reaction rate, as shown by the results of Hume and Colvin for the dehydration of potassium hydrogen oxalate hemihydrate, where the extreme thinness of the crystals permitted free escape of the liberated water molecules. On the other hand, if the nature or thickness of the layer of resultant imposes a mechanical restriction to diffusion, the pressure at the interface will increase, and the rate of reaction decrease, since Smith and Topley have shown that even small pressures of water vapour will cause a marked decrease in rate. Thus the progressive increase in thickness of the layer of monohydrate will be associated with an increasing pressure at the interface and a decreasing rate of reaction.

At this point it is advisable to recall that the extent of decomposition is measured by the weight of water lost from the reactant. Hence the true rate of reaction is obtained only if the water vapour can escape from the mass of crystals at a rate great in comparison with its rate of liberation at the interface  $\text{CuSO}_4$ .  $3\text{H}_2\text{O} - \text{CuSO}_4$ .  $\text{H}_2\text{O}$ . The possibility arises, therefore, that the apparent reaction rate may be fictitious, owing to adsorption of part of the liberated water on the monohydrate. In this way the interfacial reaction might be complete, before it became

apparent from the weight measurements.

Whilst the experiments do not at present permit of differentiation between these two views, the former seems the more reasonable. In itself, however, this is hardly sufficient to explain the extreme slowness of the rate of loss of water in the later stages of decomposition, and the difference in the magnitude of the impedance at different temperatures. In this connection, another phenomenon, known to occur, 1, 3, 5 merits This is the recrystallisation of the finely divided—pseudogaseous—monohydrate, which is the first product of the dehydration. to form larger crystalline aggregates. The effect of this process may be considerable in that when a suitable thickness of monohydrate has been formed, the recrystallisation may result in the formation of what is practically a continuous shell effectively shielding the core from further dehydration. Moreover, since the rate of recrystallisation will be increased by a rise in temperature, it is to be expected that the impedance effect will be more marked at the higher temperatures. That this behaviour is not shown to so great an extent in the dehydration of copper sulphate pentahydrate is probably due to the much greater difference in molecular volume between copper sulphate pentahydrate and monohydrate (109, 54.3) than between trihydrate and monohydrate (80, 54.3).

In conclusion the authors wish to express their thanks to Professor R. Whytlaw Gray for his encouragement during the progress of this work.

#### Summary.

- 1. An experimental study has been made of the dehydration of copper sulphate trihydrate at a series of temperatures.
- 2. The rate of propagation of the reaction  $CuSO_4$ .  $3H_2O \xrightarrow{-2H_2O} CuSO_4$ .  $H_2O$  has been determined and applied to the derivation of the energy of activation. A value of 15,600 calories per gram molecule is obtained.
- 3. Reasons have been advanced for the observed retardation of the rate as the thickness of the monohydrate shell increases.

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# ON THE PHOTOCHEMISTRY OF HYDROGEN SULPHIDE.

By N. O. Stein.

Received 2nd February, 1933.

It is well known that hydrogen sulphide gas is decomposed when illuminated with ultra-violet light of short wave-length, but the history of accurate measurements of the photolysis of hydrogen sulphide is confined to one paper by Warburg and Rump.<sup>1</sup>

<sup>&</sup>lt;sup>1</sup> E. Warburg and W. Rump, Z. Physik, 58, 291, 1929.

This paper describes experiments of a quantitative nature on the photolysis of solutions of hydrogen sulphide in hexane and in water. Apparently no quantitative work has hitherto been recorded dealing with the pure gas itself.

The present communication describes some determinations of the quantum efficiency of the photochemical decomposition of hydrogen sulphide gas and their bearing on the nature of the photo-reaction.

# Preliminary Experiments.

An apparatus (Fig. 1) was constructed with which several experiments were carried out to determine how much hydrogen is obtained from the photo-decomposition of hydrogen sulphide in a given time of illumination with the total radiation of the mercury arc. This was done in order to obtain information which would facilitate the construction of a quantitative apparatus. A streaming method was employed.

A quartz cell, with optically-faced windows, having two side tubes, was illuminated with the total radiation of a vertical type, atmospheric

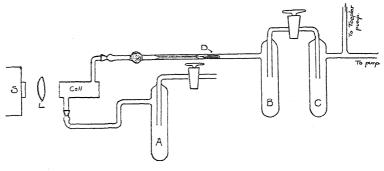


Fig 1.

pressure mercury arc lamp. The incident light was made approximately parallel by means of a quartz lens. To one of the side tubes, a gas trap A was affixed by means of a quartz-glass ground joint, sealed over with de Khotinsky cement. The other side tube was connected in the same manner to a bulb containing glass wool and to this there was sealed a device for regulating the flow of the gas. This device consisted of a capillary tube about 20 cms. long to which was sealed a piece of wide tubing. The latter contained a smaller glass tube in which a small cylinder of soft iron was enclosed and which had fused to one end a long glass rod of almost the same diameter as the capillary tube. By means of a small electromagnet this plug slid up and down the capillary, increasing or decreasing its resistance to diffusion. Beyond this device there were joined two gas traps, B and C, connected with each other through a large-bore tap, and beyond these, a Y-tube, one end of which led to a Toepler pump arranged so that the gas could be collected, and the other through a tap to a high vacuum pump.

Hydrogen sulphide gas, which was prepared, dried and frozen in a manner described previously 2 was allowed to evaporate into trap A,

<sup>&</sup>lt;sup>2</sup> C. F. Goodeve and N. O. Stein, Trans. Farad. Soc., 27, 393, 1931.

which was cooled with liquid air. The whole apparatus was then pumped out until several strokes of the Toepler pump showed a negligible amount of gas. The trap C was always immersed in liquid air. The flow of hydrogen sulphide gas now commenced from A to B and the quartz cell was illuminated with the full radiation of the mercury arc. When all the hydrogen sulphide had passed from A to B, which had been cooled with a CO<sub>2</sub>-alcohol mixture and liquid air respectively, the cooling jackets of these two traps were reversed and now the gas diffused from B to A.

The hydrogen sulphide having condensed in trap B, which was now cooled with liquid air, the tap between B and C was opened and the Toepler pump was operated until all the residual gas was collected and the vacuum had been made as high as possible. The residual gas was analysed in a Haldane apparatus.

From a number of such experiments it was found that one hour exposure resulted in the production of about 1.3 c.c. hydrogen at atmospheric pressure. It was thus evident that subsequent work would entail the handling of small amounts of hydrogen.

During these preliminary experiments it was noticed that during the illumination a yellowish glow filled the cell. In later experiments, when the incident light was almost exactly parallel and the beam was reduced to dimensions smaller than that of the area of the windows of the cell, this yellow glow had the appearance of a Tyndall cone. The glow did not appear throughout the cell as soon as it was exposed to the radiation, but developed after several seconds, starting near the window next to the source and increasing in length until it filled the total light path in the cell.

Since sulphur vapour exhibits a fluorescence spectrum between 5650 Å.U. and 2800 Å.U. when illuminated with light which falls within its band absorption system, which extends from 4000 Å.U. to 2548 Å.U.³ the following experiment was carried out to determine whether there was any visible fluorescence. The hydrogen sulphide-filled cell was illuminated with the radiation from a condensed spark discharge between iron electrodes, but between the cell and the source was interposed a screen of cobalt glass (which transmits the wave-lengths between 4000 and 3000 Å.U.) after the Tyndall beam had appeared in its full intensity. This experiment was carried out in a dark room with the cell shielded from all extraneous light. No fluorescence was observed, which indicates that solid sulphur particles of colloidal dimensions are alone responsible for the effect, and that it is not due to resonance from  $S_2$  molecules.

The appearance of the Tyndall beam is visual evidence of the photodecomposition of hydrogen sulphide gas, and shows that the decomposition is complete in the gaseous phase, and that the walls are not necessary for the recombination of sulphur atoms to form solid sulphur.

#### An Apparatus for Determining Quantum Efficiencies.

The apparatus which was finally assembled for the determination of the quantum efficiencies consisted of the following components: the light source and monochromator, the light energy measuring system, the reaction cell and reservoirs, the gauge for measuring the hydrogen produced in the photolysis, and the pumping system. These will now be described.

The Light Source.—Hydrogen sulphide begins to absorb light at about 2700 Å.U., and the absorption is continuous, increasing to a maximum in the neighbourhood of 1950 Å.U. Since it was considered desirable to have as complete an absorption as possible, it was necessary to use a condensed spark discharge between metallic electrodes as the source. Zinc electrodes were used in conjunction with a single prism, large aperture monochromator, designed by Mr. C. F. Goodeve, and constructed in these laboratories by Mr. Alliss. A fairly narrow region was isolated in the neighbourhood of 2050 Å.U., as determined spectroscopically. Only the zinc lines between 2138.5 Å.U. and 2025.5 Å.U. appeared on the plates.

The zinc electrodes were of large diameter to effect their rapid cooling. The supply current was derived from a constant voltage battery, and it was found that the source remained steady to within 10 per cent. over

the period of a run.

The Thermopile and Galvanometer System.—The thermopile used was of the Moll 80 element type. This was encased in a brass container, and was used without a window. A limiting diaphragm was used to ensure that all the light fell on the central area of the elements. When the thermopile was in use it was further encased in a thick layer of cotton wool and fitted into a wooden box. During the course of the experiments the room was thermostated roughly so that there were no considerable variations in the room temperature. The E.M.F. produced in the thermopile was balanced by means of a potentiometer circuit, after the method developed by Guild, and used with some slight modification in technique by Nagai and Goodeve. The system employed by Nagai and Goodeve was used here, except that a Zernicke high sensitivity galvanometer replaced the less sensitive one of the Moll pattern.

The calibration of the thermopile in absolute units was carried out, using a carbon filament lamp supplied and standardised by the Bureau of Standards according to their specifications. Several calibrations were made over the period of use and a remarkable constancy of the calibration

was obtained.

The Hydrogen Pressure Gauge.—Because of the desirability of working with hydrogen sulphide gas free from mercury vapour, in order to rule out any possibility of a mercury photosensitised reaction, it was impossible to use a McCleod gauge for direct measurements of the pressure of hydrogen produced in the photolysis; nor was it possible to use mercury manometers to measure the pressure of the hydrogen sulphide. The Pirani gauge, which depends on the cooling of a heated wire by the surrounding gas, was chosen as the most convenient for the purpose of the present work. It is especially sensitive for hydrogen because of the high heat conductivity of this gas. At low pressures the conductivity of a gas is a function of its pressure, and several methods are available for following the electrical effect of the pressure changes. The gauges used in the present work were obtained from the General Electric Research Laboratories, Wembley.

The Pumping System.—A two-stage Gaede mercury metal diffusion pump, backed by a "Hyvac" oil pump, was used. The pressures were read on a large-ratio McCleod gauge, and this system easily produced vacuums resulting in a "negative" pressure on the McCleod gauge

<sup>&</sup>lt;sup>4</sup> J. Sci. Instr., 7, 378, 1930. <sup>5</sup> Trans. Farad. Soc., 27, 508, 1931. <sup>6</sup> Hale, Trans. Amer. Electrochem. Soc., 20, 243, 1911; Campbell, Proc. Physic. Soc., 33, 287, 1921.

which can be taken to indicate vacuums of the order of at least 10<sup>-6</sup> mm. of mercury. The apparatus proper was protected from mercury vapour

by a large-volume liquid air trap.

The Assembled Apparatus.—The reaction cell (Fig. 2) had plane parallel optically clear windows, its length being 4 cms. and its diameter 2·54 cms. The cell was connected by means of a quartz-glass ground joint, through taps, to the trap A and to the Pirani gauge and pumping systems. All taps and joints were lubricated with a small quantity of "Apiezon" low vapour pressure grease. A palladium tube P was sealed into the apparatus in order to admit small quantities of hydrogen into the evacuated apparatus so that the Pirani gauge could be calibrated against the McCleod gauge. Immediately behind the cell, the thermopile T was mounted on a movable stand which had a vertical adjustment. In front of the cell a quartz lens and a diaphragm D were mounted to bring all the light on to the central area of the thermopile surface and to limit the beam to dimensions smaller than the area of

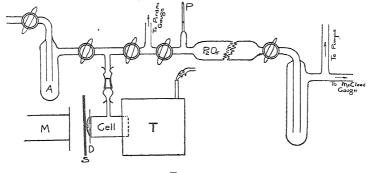


Fig 2.

the windows of the cell. A cardboard shutter S was placed between the monochromator M and the cell.

#### Experimental Procedure.

The Pirani gauge was calibrated against the McCleod gauge, using pure hydrogen, admitted through the palladium tube P by directing a small hydrogen flame against it. A series of pressure readings were taken and the corresponding voltages, which it was necessary to apply to the wheatstone bridge of which the Pirani gauge formed one arm, in order to obtain a balance as indicated by a sensitive galvanometer, were recorded on a millivoltmeter. The pressures were plotted against the relation  $(V^2 - V_0^2)/V_0^2$ , where  $V_0$  is the voltage corresponding to the highest vacuum obtainable and V that corresponding to the higher pressures of hydrogen. The points fall accurately on a straight line for low pressures.

A number of tests were carried out in order to determine whether any irregularities would occur in the measurement of the residual pressure of hydrogen. Hydrogen sulphide gas was allowed to evaporate into the quartz cell, frozen out with liquid air and the pressure read on the Pirani gauge. The tap to the gauge was then closed and the hydrogen sulphide was allowed to warm up until vaporised. It was then again

frozen out with liquid air and the pressure again recorded. In all cases it was found that the original zero pressure was obtained. This procedure was repeated with mixtures of hydrogen and hydrogen sulphide, and the original hydrogen pressure was always obtained after the

hydrogen sulphide had been frozen out with liquid air.

The method generally adopted in making a run was as follows: Pure dry hydrogen sulphide was condensed in trap A (Fig. 2), which was cooled with liquid air. The whole apparatus was evacuated until the Pirani gauge and the McCleod gauge indicated a pressure of less than 10<sup>-5</sup> mm. of mercury. The liquid air jacket was replaced by a CO<sub>2</sub>alcohol cooling mixture and the hydrogen sulphide was liquified. The trap was again cooled with liquid air, and after a few minutes the pumps were again operated. The taps on either side of the Pirani gauge were now closed. The source was started and measurements were made of the light passing through the evacuated cell by means of the thermopilegalvanometer system. A suitable cooling mixture was now placed about the trap A and the hydrogen sulphide evaporated into the cell, the temperature of the cooling agent being read on a pentane thermometer. After sufficient time had elapsed for equilibrium to occur between the liquid hydrogen sulphide and its vapour, the tap between A and the cell was closed. The shutter was now opened and the photo-decomposition commenced. The time of irradiation was recorded on a stop-watch and energy measurements were made continuously, although for most experiments there was complete absorption. After sufficient time had elapsed for the production of a suitable pressure of hydrogen, determined during trial runs, the source was cut off and the cell immersed in liquid air to a given height on its quartz entrance tube. The residual hydrogen pressure was then measured with the Pirani gauge, the tap between the cell and this gauge being opened.

#### The Dark Reaction.

To test whether there was any dark reaction, that is, whether there was any decomposition resulting in the production of hydrogen when the cell was not illuminated with the wave-lengths absorbed by hydrogen sulphide, the following experiment was carried out. The cell and its content of hydrogen sulphide was illuminated by the light from a spark source, but a screen of clear plate glass was interposed between the source and the cell. Long exposures were made and the cell was immersed in liquid air. The residual pressure determined with the Pirani gauge proved to be zero and the conclusion to be drawn is that there is no dark reaction detectable with the system used. The Tyndall beam did not appear during these illuminations.

## Experimental Results.

In calculating the light-energy values the reflection-absorption factor for the rear window of the cell, which was found to be 15 per cent. for the wave-length region used, was taken into account. The temperature difference between the quartz cell immersed in liquid air and the Pirani gauge at room temperature was also taken into account in calculating the number of molecules of hydrogen produced. With the size of tube used to connect the cell and gauge there could be no thermal transpiration

effect and the pressure was the same throughout the system. The ratio of the number of molecules in the cold and warm parts of the system is found by using the equation n/n' = VT'/V'T, where n and n' are the number of molecule in each side of the system whose respective volumes and temperatures are V and V' and T and T'.

The hydrogen pressures were determined with an accuracy of at least 5 per cent., as determined from the Pirani gauge calibration curves. The quantum efficiencies have a possible error of 15 per cent. The hydrogen sulphide pressures were found from the vapour pressure curve after determining the temperature of the cooling agent surrounding the trap A (Fig. 2) and are to be considered approximate.

Table I shows the results of the experiments with different pressures

of hydrogen.

TABLE	IMEAN	Wave-Length	OF	ILLUMINATION,	2050 Å.U.
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Time of Illumina-	No. of Molecules of Hydrogen.	No. of Quanta Absorbed.	Hydrogen Molecules No. of Quanta	Pressure of H <sub>2</sub> S.
720 secs. 900 ,, 420 ,, 720 ,, 720 ,, 720 ,, 720 ,, 720 ,, 720 ,, 720 ,,	$\begin{array}{c} 43.7 \times 10^{15} \\ 45.8 \times 10^{15} \\ 21.9 \times 10^{15} \\ 23.7 \times 10^{15} \\ 25.5 \times 10^{15} \\ 25.5 \times 10^{15} \\ 25.5 \times 10^{15} \\ 21.9 \times 10^{15} \\ 25.5 \times 10^{15} \end{array}$	$\begin{array}{c} 11.6 \times 10^{15} \\ 14.5 \times 10^{15} \\ 6.8 \times 10^{15} \\ 11.7 \times 10^{15} \end{array}$	3.8 3.2 3.2 2.0 2.2 2.2 2.2 1.9 2.2	1350 mm. 1350 ,, 900 ,, 250 ,, 250 ,, 250 ,, 125 ,, 175 ,,

#### Discussion.

A consideration of the last two columns in Table I shows that for pressures of about 250 mm. of mercury and lower, the number of hydrogen molecules produced for each quantum of energy absorbed is approximately 2. With higher pressures the number of molecules of hydrogen increases to 3.8. In order to examine the meaning of these results it is necessary to assume some primary process. The absorption spectrum of hydrogen sulphide, being completely continuous in character so far as it has been investigated, indicates according to spectroscopic theory that a dissociation of the molecule is the direct consequence of the absorption of light. There are three principal ways in which dissociation might take place. These can be represented by the following equations:

$$H_2S = H + H + S$$
 . . . (1)  
 $H_2S = H_2 + S$  . . . (2)  
 $H_2S = H + HS$  . . . . (3)

It is necessary to consider the energetics of these processes in order to decide on their value.

A complete dissociation into atoms can be ruled out at once, since it is necessary to supply 174.7 Cals. of energy to effect this process. This energy corresponds to light of wave-length 1700 Å.U. (59,000 wave numbers). Nhv for 2050 Å.U. corresponds to 138.7 Cals.

<sup>&</sup>lt;sup>7</sup> Reynolds, Phil. Trans., 170, ii, 727, 1879; Jeans, Dynamical Theory of Gases 1925 ed., pp. 122-123.

The energetics of the second and third possibilities, assuming the production of normal products, can be calculated, using the following data:—8

$$\begin{array}{l} \text{H}_2 \text{S} = \text{H} + \text{H} + \text{S} - \text{I74·7 Cals.} \\ \text{H}_2 \text{S} = \text{H}_2 + \frac{1}{2} \text{S}_2 \text{ (gas)} - \text{I9·6 Cals.} \\ \text{H}_2 \text{O} = \text{H} + \text{H} + \text{O} - \text{219 Cals.} \\ \text{H}_2 \text{O} = \text{H} + \text{OH} - \text{I03 Cals.} \\ \text{OH} = \text{H} + \text{O} - \text{I16 Cals.} \\ \frac{1}{2} \text{S}_2 \text{ (gas)} = \text{S} - \text{51·3 Cals.} \\ \text{H}_2 = \text{H} + \text{H} - \text{I03 Cals.} \\ \end{array}$$

From the above equations a mean value of 71.5 Cals is found for process 2. The value for process 3 cannot be computed directly, as data for the HS molecule do not exist, but by analogy to water vapour an estimated value of 82.3 Cals. is obtained. Since these values correspond to light in the regions 4000 Å.U. and 3500 Å.U. and absorption by hydrogen sulphide does not become appreciable until 2700 Å.U., the excess of energy must be accounted for. From spectroscopic evidence alone, taking into account the value for the threshold of absorption, Goodeve and the author suggested that process 2 might be possible if the sulphur atom existed in the metastable ID state. Assuming that process 3 were possible, the excess energy could be contained in an unknown excited HS molecule or it could be translational energy of the products.

In accounting for the observed quantum efficiency of about 2 at the lower pressures, the second process can be explained by the following reactions:—

$$H_2S + h\nu = H_2 + S^*$$
  
 $S^* + H_2S = H_2 + S_2$ 

The increased efficiency observed for higher pressures could then be explained by the production of further S atoms resulting from collisions between sulphur molecules, having a large translational energy, with  $\rm H_2S$  molecules. These S atoms could then react with  $\rm H_2S$  molecules, producing hydrogen molecules.

Infra-red analysis has shown that the hydrogen sulphide molecule is triangular, and that the hydrogen atoms are not bound together in the molecule. The initial effect of absorption must result in the splitting off of both hydrogen atoms simultaneously according to process 2. Although it is difficult to conceive of the decomposition of the hydrogen sulphide molecule in this way, similar processes have been postulated.<sup>9</sup>

Process 3 assumes the existence of HS molecules. Although no evidence of their existence has yet been recorded, there is no reason why they should not exist. The observed quantum efficiencies could be accounted for on the basis of process 3 by the following scheme:—

$$H_2S + h\nu = H + HS$$
  
 $H + H_2S = H_2 + HS$   
 $HS + HS = H_2 + S_2$ 

and again the higher quantum efficiencies at increased pressures are explained by collisions between S<sub>2</sub> and H<sub>2</sub>S.

<sup>Kassel, Kinetics of Homogeneous Gas Reactions; Christy and Naude, Physic.
Rev., 37, 903, 1931; International Critical Tables.
Kirkbride and Norrish, Trans. Farad. Soc., 27, 404, 1931.</sup> 

The problem cannot be solved unambiguously by quantum efficiency measurements alone and attempts are now being made to identify the products of the *primary* reaction.

The author wishes to thank Mr. C. F. Goodeve for his kind criticism and advice and the Department of Scientific and Industrial Research for a Senior Award during the tenure of which this work was carried out.

## Summary.

The photo-decomposition of hydrogen sulphide gas has been investigated. Preliminary experiments showed that visual evidence of the decomposition is afforded in the production of a Tyndall beam, due to the production of colloidal sulphur particles, when the gas is illuminated in its absorption region. Quantum efficiency measurements were made, using monochromatic light of 2050 Å.U., at various pressures. The nature of the primary process has been discussed.

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### REVIEW OF BOOK.

Chemical Analysis of Iron and Steel. By G. E. F. LUNDELL, Ph.D., J. I. HOFFMAN, Ph.D., and H. S. BRIGHT, M.S. (New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd., 1931. 42s. net.)

Although it is still true to say that steelmaking is largely an art which depends considerably for its success on the personal skill of the steel melter, it is also an art which is being controlled by science to an ever increasing extent. The first application of science in the steelmaking industry consisted in determining the chemical composition both of the product and of the raw materials used in its manufacture and, although the chemist has to some extent been overshadowed by the physicist in the later developments of scientific metallurgy, the determination of the chemical composition of steel during its manufacture is still the basis of modern steelmaking. The properties of a finished steel product are a function of its composition and the treatment, thermal and mechanical, it has received; the former must be known before the treatment can be made effective. The importance of chemical analysis in the steel industry is therefore unquestionable.

Most steelmaking processes are refining processes, as a result of which the steelmaker endeavours to produce material having a certain desired composition. In order that he may judge how his operations are progressing, it is necessary that he should know quickly, at any time, the composition of the bath of molten steel under his charge. The steelworks chemist is therefore called upon to analyse rapidly samples sent to him and to be able to report within a few minutes the contents of certain elements in these samples to an accuracy of possibly o'o' per cent. The analytical methods he uses must therefore be rapid and accurate.

Furthermore, the increasing use of alloy steels and the variety of alloying metals used for the purpose of conferring desired properties on steel has complicated the chemist's task very considerably. Several alloys may be present together and hence the methods the chemist employs for a particular metal must be valid

in the presence of the other alloying metals. If they are not universally valid, the chemist must know their limitations and what modifications must be adopted to eliminate the effect of interfering metals. The chemist must also be able to analyse the ferro-alloys which are used for adding these various metals to steel and also, very frequently, the ores from which they are derived as well as iron ore itself. And it does always follow that a method suitable for determining a small amount of a metal in steel is equally adapted for determining the larger amounts of the same metal present in its ore or in the ferro-alloy made from the latter. The material with which a steelworks chemist has to deal is therefore very varied and when to the list already given are added such sundries as coal and other fuels, slags produced in steelmaking operations and the fluxes and other minerals used in modifying these slags, it is not surprising to find that he may have to determine, at one time or another, at least one-half of the known elements.

In preparing a comprehensive treatise dealing with the numerous analytical methods which have been developed by chemists to obtain accuracy and speed in determining the composition of such a wide range of materials, the authors of this excellent book have done much more than merely cataloguing approved methods of analysis. Besides describing the procedure to be adopted in each case, they discuss the applicability of each particular method, the possible interference of other metals, if this can be eliminated and how. As a result of this detailed information, and there is a mass of it in the book, analysts will be able to determine whether a given method is suitable or not for some particular type of steel. The authors also distinguish between methods adapted more particularly for rapid routine work and others more suitable for analyses of the highest precision (e.g. for referee work), in each case discussing the probable accuracy to be obtained by a competent analyst.

It was mentioned above that the work of the chemist has been somewhat overshadowed by that of the physicist, during the last few decades, in the development of scientific metallurgy. In one respect at least, however, the chemist is taking a prominent place; modern research has indicated the great influence which non-metallic impurities almost certainly exert on the physical properties of the steel which contains them. The determination of the character and amount of these inclusions is an enormously difficult problem to the solution of which chemical analysis is likely to render great assistance. It is evidence of the comprehensive and up-to-date-character of the authors' work that they include a chapter describing the most recently developed methods for the determination of hydrogen, nitrogen, oxygen, and the various oxides unavoidably or accidentally present in steel.

As a whole, the book is a notable addition to the literature on analytical chemistry and one which should be studied by all who are concerned in any way with the analysis of ferrous materials.

J. H. G. M.

# THE EXTENT OF DISSOCIATION OF ZINC SUL-PHATE.

By Irving A. Cowperthwaite.

Received 13th February, 1933.

A series of papers by Cecil W. Davies and his co-workers have appeared in this journal 1 in which dissociation constants for many salts of varying valence types have been evaluated. Dissociation constants for a number of (2, -2) salts were given in the first and fourth numbers of this series. Among these values, a dissociation constant equal to 0.0045 was given for zinc sulphate. The present author has studied galvanic cells involving this salt at high dilution 2 and found that the electromotive force measurements could be satisfactorily interpreted on the assumption that the zinc sulphate was completely dissociated in dilute solution (from 0.01 m. to 0.0005 m.). These two different conclusions that were drawn concerning the extent of dissociation of zinc sulphate are so divergent that it would be of interest to examine the bases upon which they rest.

The dissociation constants communicated by Davies were obtained by treatment of conductance data. The calculations involved require functional relationships between the activity co-efficient and concentration and between the conductance and concentration.

In expressing the activity coefficient as a function of the concentration. Davies uses the relationship  $-\log f^{\pm} = A\sqrt{c}$ . Although this expression is of the form of the Debye-Hückel limiting law, A is an adjustable constant rather than the value calculated from fundamental constants according to the theory. The empirically determined value of A is 3.7 in the case of zinc sulphate whereas the theoretical value of A for a (2, -2) electrolyte is 4.05 at 25°.\*

The limiting law of Debye and Hückel may be used satisfactorily in the simple case of a uni-univalent electrolyte at high dilution, but it has been found to be quite inadequate for high valence type electrolytes,

39 593

<sup>&</sup>lt;sup>1</sup> I. C. W. Davies, *Trans. Faraday Soc.*, **23**, 351, 1927. II. E. C. Righellato and C. W. Davies, *ibid.*, **26**, 592, 1930. III. W. H. Banks, E. C. Righellato, and C. W. Davies, *ibid.*, **27**, 621, 1931.

IV. R. W. Money and C. W. Davies, *ibid.*, 28, 609, 1932.

<sup>2</sup> I. A. Cowperthwaite and V. K. La Mer, J. Amer. Chem. Soc., 53, 4333, 1931.

<sup>&</sup>lt;sup>3</sup> P. Debye and E. Hückel, *Physik. Z.*, 24, 185, 1923.

\* Money and Davies (1, IV) give the limiting form of the Debye-Hückel theory for a (2, -2) electrolyte at  $25^{\circ}$  as  $-\log f^{\pm} = 2.84$ .  $\sqrt{c_i}$ . The numerical value in this expression differs from that just given because  $c_i$  refers to the concentration of ions. If the concentration of salt is used, the coefficient must be multiplied by  $\sqrt{2}$ . The empirical slope found by Davies was for 18°. For comparison with the value at 25°, it should probably be increased by five or six hundredths units, but such a correction is of secondary importance for the purpose of this discussion.

such as the bi-bivalent case, even at great dilution. It was pointed out by La Mer 4 that the inadequacy of the Debye-Hückel theory under these conditions was probably due in large measure to a mathematical approximation introduced by these authors in the development of their theory. They solved the Poisson equation after retaining only the linear term resulting from the expansion of the Boltzmann exponential expression for the density of electricity. Gronwall, La Mer and Sandved 5 have pointed out that this approximation frequently leads to error, particularly when dealing with high valence type electrolytes, solvents of low di-electric constant, and electrolytes having a small value of the ion size parameter "a." The latter authors give a complete analytical solution of the Poisson-Boltzmann equation in terms of a series, and furnish numerical tables permitting evaluation of the activity coefficient through the fifth approximation for the cases of symmetrical valence type electrolytes.6

In the accompanying table, activity coefficients for a (2, -2) electrolyte at 25° are compiled for comparison. The concentrations to which the activity coefficients apply are given in the first column; coefficients computed using Davies' empirical slope are given in the second; those obtained from the Debye-Hückel limiting law in the third; values calculated on the basis of the extended theory of Gronwall, La Mer and Sandved using an ion size of 3.64 Å in the fourth; and the experimentally determined values of the activity coefficient of zinc sulphate are given

in the fifth column.

C.	Davies.	D.H.L.L.	G. L. & S. a = 3.64  Å.	ZnSO <sub>4</sub> . Observed.
0.0005	0.831	0·812	0·780	0·780
0.001	0.769	0·744	0·701	0·700
0.002	0.690	0·659	0·608	0·608
0.005	0.556	0·517	0·478	0·477
0.01	0.437	· 0·393	0·386	0·387

These activity coefficients are presented graphically in the accompanying figure. Reference to the table shows that the empirical expression used by Davies does not give activity coefficients agreeing with either the complete solution of the Debye-Hückel theory or the measured values for ZnSO<sub>4</sub>. Furthermore, the figure shows that the logarithm of the activity coefficient of ZnSO<sub>4</sub> is not a linear function of  $\sqrt{c}$ . These observations make it questionable if an expression for the activity coefficient of a (2, -2) electrolyte patterned after the Debye-Hückel limiting law is a legitimate approximation.

If now we turn our attention to the functional relationship between the conductance and concentration, we find that Davies uses the Onsager equation.7 The Onsager equation is strictly a limiting law.

<sup>&</sup>lt;sup>4</sup> V. K. La Mer and C. F. Mason, J. Amer. Chem. Soc., 49, 410, 1927; V. K. La Mer, Trans. Amer. Electrochem. Soc., 51, 507, 1927.
 T. H. Gronwall, V. K. La Mer and K. Sandved, Physik. Z., 29, 358, 1928.

V. K. La Mer, Annual Survey of American Chemistry, 5, pp. 17-18, 1930.

<sup>6</sup> V. K. La Mer, T. H. Gronwall, and L. J. Greiff, J. Physic. Chem., 35, 2245, 1931, deal with the case of unsymmetrical valence type electrolytes and give tables which make possible evaluation of the activity coefficient through the third approximation. <sup>7</sup> L. Onsager, Physik. Z., 27, 388, 1926; 28, 277, 1927.

Even in the simple case of a (I, -I) electrolyte, the Onsager equation holds only at great dilution. Whether or not the Onsager equation approximates the behaviour of a high valence type electrolyte, such as a (2, -2) salt, is not known. We should need a (2, -2) salt that was clearly completely dissociated in order to test the equation under these conditions. The Onsager equation rests on the same basis as the Debye-Hückel theory. Both seek to evaluate the departure from ideal behaviour by considering the electrostatic forces between the ions. The Debye-Hückel limiting law is useful in the case of a (I, -I) salt, but it fails to account for the higher valence types such as the (2, -2) type. Similarly, the Onsager equation gives the limiting slope to which data on (I, -I) electrolytes approach, but it is very possible that the

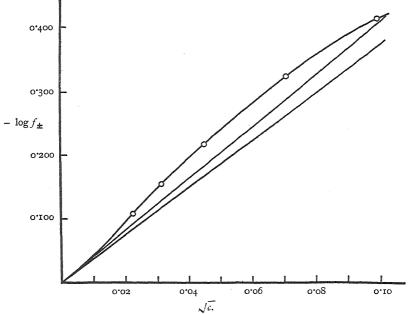


Fig. 1.—The lower straight curve shows Davies' empirical slope for ZnSO<sub>4</sub>, and the centre curve is the Debye-Hückel limiting slope for a (2,-2) electrolyte. The third curve shows the Gronwall, La Mer and Sandved extension of the Debye-Hückel theory for a (2,-2) electrolyte using an ion size 3·64 Å. The circles indicate the measured values of the activity coefficients for ZnSO<sub>4</sub>.

same type of mathematical approximations that invalidate the Debye-Hückel limiting law for high valence types would also seriously weaken the Onsager equation in its interpretation of these same electrolytes. Reference to the figure will show that deviations between the limiting law and the complete solution of the Debye-Hückel theory for (2,-2) salts occur at high dilution and such discrepancies might readily be expected in the case of the Onsager equation under the same circumstances.

The table contains values for the activity coefficient of  $ZnSO_4$  obtained from measurements of the electromotive force of the cell  $Zn-Hg/ZnSO_4(m)$ ,  $PbSO_4(s)/Pb-Hg$ ; and also values of the activity coefficient of a (2, -2) electrolyte calculated by means of the extended

Debye-Hückel theory using an ion size of 3.64 Å. The two sets of values are in complete agreement. One of the basic assumptions of the Debve-Hückel theory is that the electrolyte is completely dissociated. The fact that activity coefficients calculated from a theoretical expression based on the postulate of complete dissociation agree quantitatively with those obtained from experimental measurements is evidence in favour of complete dissociation. The ion-size of 3.64 Å which was used in these computations is quite arbitrary, being selected so as to yield the best agreement between theory and experiment, but it is a reasonable value in the light of crystal structure data. The value of the ionsize parameter, or the distance of closest approach for the ions of zinc sulphate, can be estimated in the following manner. The distance between the centres of a zinc ion and a hexavalent sulphur ion with one oxygen ion on the line of centres between may be obtained from the tables given by Goldschmidt.8 It is found to be equal to 3.83 Å (Pauling) or 3.81 Å (Goldschmidt). These distances represent maximum distances of closest approach of the zinc and sulphate ions. The probable configuration of the sulphate ion would make a somewhat smaller value, such as the one actually used, entirely reasonable.

Ability of the Debye-Hückel theory to interpret the behaviour of electrolytes quantitatively is generally conceded to be one of the strongest supports of the complete dissociation theory. On the basis of this test, zinc sulphate gives evidence of being completely dissociated. Some work now in progress in these laboratories is of interest as it bears on the validity of the Debye-Hückel theory as a criterion of complete dissociation. Mr. J. Barksdale has been measuring the electromotive force of galvanic cells involving the electrolyte thallous chloride which is generally accepted as an incompletely dissociated salt. Davies gives a dissociation constant for the thallous chloride equal to 0.3, which would mean that thallous chloride was a far stronger electrolyte than zinc sulphate which is given the dissociation constant of 0.0045. Yet the extended form of the Debye-Hückel theory accounts for the data on zinc sulphate quantitatively, and at the same time is unable to interpret the data on the thallous chloride. The Debye-Hückel theory would tend to show that zinc sulphate was a far stronger electrolyte than thallous chloride. In fact it would tend to favour the idea that zinc sulphate can be considered completely dissociated up to 0.01 m.

The discussion in this paper has been restricted to the one salt, zinc sulphate, as that is a salt that the author has studied in sufficient detail. However, everything said applied equally well to cadmium sulphate which has been studied by La Mer and Parks.9 It is not the purpose of this paper to assert dogmatically that these sulphates are completely dissociated, but to show that there is very real evidence pointing to that conclusion, and also to point out that much of the evidence that has been assembled against this hypothesis has been based upon incomplete theoretical treatment.

<sup>&</sup>lt;sup>8</sup> V. M. Goldschmidt, Trans. Far. Soc., 25, 253, 1929, see p. 282. <sup>9</sup> V. K. La Mer and W. G. Parks, J. Amer. Chem. Soc., 53, 2040, 1931, and further work by these authors on cadmium sulphate to appear in the same journal.

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# THE VERIFICATION OF A MECHANISM INVOLV-ING A REACTIVE INTERMEDIATE COMPOUND. THE RATE OF OXIDATION OF OXALATE BY HYPOBROMOUS ACID.

By Benjamin Makower and Herman A. Liebhafsky.

Received 27th Fanuary, 1933.

In 1905 Bray 1 was able to show that the kinetic behaviour of the halogens, X<sub>2</sub>, in aqueous solution could usually be explained in terms of a mechanism involving the hypohalous acid, HXO (or its ion XO<sup>-</sup>) as reactant or resultant in a rate-determining step. Although X, has no direct kinetic rôle in such a mechanism, its concentration (or that of some derived complex ion like X<sub>3</sub>-) often appears in the rate law: for the equilibria

$$X_2 + H_2O \rightleftharpoons HXO + H^+ + X^-$$
 . . (I)  
 $HXO \rightleftharpoons H^+ + XO^-$  . . . (2)

are usually maintained. Thus the rate of the reaction at which hydrogen peroxide is oxidised in the reaction

$$X_2 + H_2O_2 = 2H^+ + 2X^- + O_2$$
 . (3)

is given by the expression 2

$$-\frac{d(H_2O_2)}{dt} = k'' \frac{(X_2)}{(H^+)(X^-)} (H_2O_2), \quad .$$
 (4)

which corresponds to the rate-determining step 2

$$HXO + H_2O_2 \rightarrow H^+ + X^- + O_2 + H_2O.$$
 (5)

If this mechanism is correct, the rate at which hydrogen peroxide reduces the pure hypohalous acid should be

$$-\frac{d(H_2O_2)}{dt} = k''/K' \text{ (HXO)(H}_2O_2).$$
 (6)

(K') is the equilibrium constant for the  $X_2$  hydrolysis, Equation 1.) So long as Reaction 5 has not been studied in the (virtual) absence of  $X_2$ , the mechanism of Reaction 3 is capable of further verification, which results when the specific rate of Reaction 5 in the absence of  $X_2$  is found to equal the quotient k''/K'. We know of no reaction involving a reactive intermediate compound in equilibrium with other substances for which the mechanism has been thus verified: experimental conditions under which such verification may be obtained are usually difficult to find.

 $<sup>^1</sup>$  Bray, Z. physik. Chem., 54, 465, 1906.  $^2$  By ( ) is meant "concentration of," unless the activity of hydrogen ion, denoted by  $a_{\rm H^+}$ , is thus enclosed; the units are always moles per litre.  $\rightarrow$  will be restricted to reactions which may be rate-determining.

<sup>&</sup>lt;sup>3</sup> That the rate law, Equation 4, may be interpreted in terms of various mechanisms, of which some may involve X<sub>2</sub>, has been pointed out by Liebhafsky, J. Amer. Chem. Soc., 54, 3499, 1932.

Debye-Hückel theory using an ion size of 3.64 Å. The two sets of values are in complete agreement. One of the basic assumptions of the Debve-Hückel theory is that the electrolyte is completely dissociated. The fact that activity coefficients calculated from a theoretical expression based on the postulate of complete dissociation agree quantitatively with those obtained from experimental measurements is evidence in favour of complete dissociation. The ion-size of 3.64 Å which was used in these computations is quite arbitrary, being selected so as to yield the best agreement between theory and experiment, but it is a reasonable value in the light of crystal structure data. The value of the ionsize parameter, or the distance of closest approach for the ions of zinc sulphate, can be estimated in the following manner. The distance between the centres of a zinc ion and a hexavalent sulphur ion with one oxygen ion on the line of centres between may be obtained from the tables given by Goldschmidt.8 It is found to be equal to 3.83 Å (Pauling) or 3.81 Å (Goldschmidt). These distances represent maximum distances of closest approach of the zinc and sulphate ions. The probable configuration of the sulphate ion would make a somewhat smaller value, such as the one actually used, entirely reasonable.

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 . . . (3)

is given by the expression 2

$$-\frac{d(\mathbf{H_2O_2})}{dt} = k'' \frac{(\mathbf{X_2})}{(\mathbf{H^+})(\mathbf{X^-})} (\mathbf{H_2O_2}), \quad . \tag{4}$$

which corresponds to the rate-determining step 2

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If this mechanism is correct, the rate at which hydrogen peroxide reduces the pure hypohalous acid should be

$$-\frac{d(H_2O_2)}{dt} = k''/K' \text{ (HXO)(H}_2O_2).$$
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(K' is the equilibrium constant for the X2 hydrolysis, Equation 1.) So long as Reaction 5 has not been studied in the (virtual) absence of  $X_2$ , the mechanism of Reaction 3 is capable of further verification, which results when the specific rate of Reaction 5 in the absence of  $X_2$ is found to equal the quotient k''/K'. We know of no reaction involving a reactive intermediate compound in equilibrium with other substances for which the mechanism has been thus verified: experimental conditions under which such verification may be obtained are usually difficult to find.

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be restricted to reactions which may be rate-determining.

3 That the rate law, Equation 4, may be interpreted in terms of various mechanisms, of which some may involve X<sub>2</sub>, has been pointed out by Liebhafsky, J. Amer. Chem. Soc., 54, 3499, 1932.

Such additional proof of mechanism was sought in this laboratory for the oxidation of hydrogen peroxide by chlorine, for which a mechanism analogous to Reaction 5 had been postulated. When hypochlorous acid and hydrogen peroxide were mixed, however, values approximately one-millionth the quotient k''/K' were obtained.<sup>5</sup> It was impossible to decide whether this anomalous result was due to a peculiarity of this one reaction or to a flaw in the general theory of the mechanism of halogen reactions; in the hope of deciding this question, the investigation of similar reactions was undertaken.

The first reaction to be thus investigated was the oxidation of hydrogen peroxide by hypobromous acid. Although accurate measurements proved impossible because the reaction was too rapid, it could be established that its specific rate at o° was not less by more than a power of ten than the value  $6.2 \times 10^{-4}/6 \times 10^{-10} = 1 \times 10^6$  found by Bray and Livingston.<sup>6</sup> While this agreement established beyond reasonable doubt that the oxidation of hydrogen peroxide by bromide does proceed through HBrO, still it appeared desirable to find a reaction for which quantitative verification could be secured.

Such a reaction is the oxidation of oxalate by bromine,

$$Br_2 + H_2C_2O_4 = 2CO_2 + 2H^+ + 2Br^-,$$
 (8)

which has been thoroughly investigated by Griffith, McKeown and Winn, who give for the rate-determining step

$$HC_2O_4^- + HBrO \rightarrow H_2O + 2CO_2 + Br^-$$
. (9)

Our results, to be presented here, quantitatively verify this mechanism and indicate that a second rate-determining step

$$HC_2O_4^- + BrO^- \to HCO_3^- + Br^- + CO_2$$
 . (10)

is possible in basic solution.

The preparation of hypobromous acid proved a matter of some difficulty. Our experience 8 indicates that pure solutions of the substance cannot be prepared by distillation because it decomposes into bromate, bromide, and hydrogen ions. Consequently, the acid was prepared by adding bromine water to the reaction mixtures, in which the hydrolysis equilibrium of bromine (cf. Eq. 1) was, for practical purposes, displaced completely to the right by removal of hydrogen and—in most cases—of bromide ions.

## Experimental Method.

A glass-stoppered 500 c.c. Erlenmeyer flask containing all the reaction mixture except the bromine was placed in a thermostat. As soon as temperature equilibrium had been attained, I c.c. of bromine solution was added, initial time being taken as the flask was shaken to secure thorough mixing. After the flask had been returned to the

<sup>&</sup>lt;sup>4</sup> Livingston and Bray, J. Amer. Chem. Soc., 47, 2069, 1925.

Bray, Chem. Rev., 10, 175, 1932.

Bray and Livingston, J. Amer. Chem. Soc., 50, 1654, 1928.

Griffith, McKeown and Winn, Trans. Far. Soc., 28, 107, 1932. Reactions and 9 are peculiarly suited to this kind of investigation since the specific rate of Reaction 9 is not very great, and since a small, but definitely known, concentration of HC<sub>2</sub>O<sub>4</sub>- can be maintained in equilibrium with oxalate ion.

8 Liebhafsky and Makower, submitted for publication in the Journal of

Physical Chemistry.

bath, 20 c.c.-pipetfuls of reaction mixture were withdrawn from time to time and blown into the quenching solution, which contained 0.03 N potassium iodide and sufficient acid to make the final (H<sup>+</sup>) 10<sup>-6</sup> M. The time at which the pipet was half emptied was recorded as the time of the sample. The samples thus obtained were titrated immediately  $^9$  with 0.004 N thiosulphate, starch being used as indicator. We shall assume that the iodine thus titrated measures the concentration of hypobromous acid: since this acid is very weak  $^{10}$  (and (BrO-) consequently very small), since bromate will not react with moderate concentrations of iodide at this low (H<sup>+</sup>), $^{11}$  and since no appreciable amount of bromine was ever present in our reaction mixtures, this assumption appears justified. The progress of Reaction  $^9$  may thus

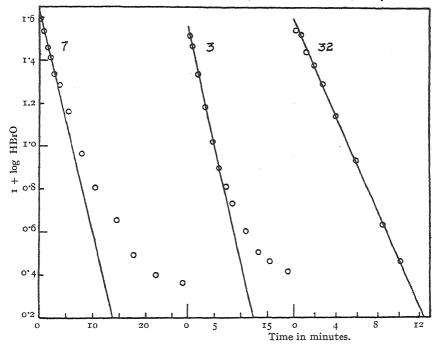


Fig. 1.—Detailed results of Experiments 7, 3 and 32 (see Table I). The concentration units for HBrO are c.c. of  $\cdot 004~N$  thiosulphate for 20 c.c. of reaction mixture.

be followed by determining the decrease with time in the amount of iodine liberated by a definite volume of reaction mixture.

The amount of hypobromous acid in these reaction mixtures was always relatively small (cf. Fig. 1); it was possible, therefore, by use

<sup>&</sup>lt;sup>9</sup> Immediate titration is imperative if the reaction between iodine and oxalate, which is sensitive to light, is to be avoided. Blank determinations in the presence of oxalate proved the method of titration used to be satisfactory—no iodine reacted with oxalate in the time (usually less than a minute) required for the titration with thiosulphate.

<sup>&</sup>lt;sup>10</sup> No accurate value for K, the dissociation constant of hypobromous acid, is available; we have chosen  $K = 10^{-9}$ , a value intermediate between  $7(10^{-8})$ , the constant for HClO (Sand, Z. physik. Chem., 48, 610, 1904), and  $2(10^{-11})$ , that for HIO (Fürth, Z. Elektrochem., 28, 57, 1922).

 $<sup>^{11}</sup>$  R. H. Clark, J. Physic. Chem., 10, 679, 1906. It has been pointed out (Ref. 8) that (BrO<sub>3</sub>-) in these reaction mixtures was always small, say 10<sup>-5</sup> M, and constant during an experiment.

of a potassium phosphate buffer solution 12 and an excess of potassium oxalate, to maintain  $(a_{\rm H}+)$  and  $(C_2O_4^{--})$  (practically) constant during the course of each experiment; (HBrO), however, decreased from an initial value of  $5 \times 10^{-4}$  almost to zero as the experiment neared completion.

TABLE I.—RATE MEASUREMENTS IN POTASSIUM PHOSPHATE BUFFER SOLUTIONS.†

Run No.	(H <sub>2</sub> PO, _)102.	(HPO4 _ )103,	$(a_{ m H}^{}+)$ 107.	(C <sub>2</sub> O <sub>4</sub> - 7).	(Br <sup>-</sup> )10 <sup>9</sup> .‡	μ <sub>c</sub> .	, . , .	$K_2 \times 10^5$ .	$k \times 10^{-3}$
					rature o°.	<u></u>			
30 13* 8 32 3* 7* 10 33 12 28* 26* 31 24* 29	4·49 4·49 4·23 3·99 3·72 3·74 3·25 2·50 1·25 0·51 0·52 0·52	0·51 0·76 1·01 1·28 1·26 1·75 2·50 3·75 4·29 4·48 4·48	15.6 15.6 9.23 6.84 6.30 5.30 3.56 1.94 1.43 0.693 0.356 0.235 0.232	0.0145 0.0145 0.0247 0.0296 0.075 0.0372 0.060 0.075 0.141 0.141 0.141 0.141	3 3 4 5 5 × 10 <sup>5</sup> 2 × 10 <sup>6</sup> 5 8 10 10 10 10	0·105 0·140 0·160 0·300 0·300 0·300 0·188 0·265 0·323 0·535 0·550 0·560 0·563	0·358 0·359 0·309 0·252 0·266 0·299 0·247 0·306 0·213 0·338 0·267 0·166 0·474 0·205	17-6 17-6 19-2 20-2 24-7 21-3 23-5 25-0 28-2 29-4 29-4 29-4	2·8 2·6 2·6 1·4‡ 1·6‡ 2·7 3·4 4·3 4·7 8·1 9·2 15·8 18·4 18·1
				Tempera	ature 5.2°.				
34 35	4.00 3.25	1.75	6·40 3·32	0.0396		0·130 0·205	0·358 0·355		5·1 5·6
				Tempera	ture 10.5°				
36 37	4·00 3·25	1.75	6.00 2.98	0.0097		0.100	0.310		
				Tempera	ture 15·3°				
38 39	4.00 3.25	1.00	5.64 2.81	0.0047 0.0097		0.085	0.251	14.1	13.5
				Tempera	ture 21.0°				
40 41	4.00 3.25	1.75	5·64 2·76	0.00345		0.108 0.081	0.331 0.331	13.2	23·4 24·8

<sup>\*</sup> Experiments marked thus were carried out in the diffuse daylight of the laboratory; in all others light was excluded.

<sup>†</sup> Except in Nos. 3 and 7, Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and AgBr were present as solids; under these conditions and at o° (Br-) =  $2.6 \frac{(10^{-8})\sqrt{(C_2O_4-7)}}{(10^{-8})\sqrt{(C_2O_4-7)}}$ ; the proportionality  $\frac{\sqrt{(2.5 \times 10^{-14})^2}}{9.4 \times 10^{-13}}$  in which the numerator constant is given by the expression represents  $[(Ag^+)(Br^-)]^2$  and the denominator  $[(Ag^+)^2(C_2O_4^-)]$ ; values at o° as for both solubility products were obtained by extrapolation of values for higher temperatures. Ag<sub>3</sub>PO<sub>4</sub> does not precipitate under the conditions in Table I. For every experiment in this table all concentrations are the arithmetical means of initial and final values.

<sup>†</sup> Approximate values only.
<sup>12</sup> Cohn, *J. Amer. Chem. Soc.*, **49**, 173, 1927.

The detailed results of several such experiments are given in Fig. 1, in which log (HBrO) for certain reaction mixtures, whose composition is listed in Table I, is plotted as ordinate against the time. For the reaction mixture (No. 32) to which Ag<sup>+</sup> had been added, the rate law

$$-\frac{d(\text{HBrO})}{dt} = k'(\text{HBrO}) \qquad . \qquad . \qquad . \tag{11}$$

is valid for the entire concentration range. (k' is a first-order constant, obtained by multiplying slopes like those in Fig. 1 by  $2\cdot 303$ .) For the other experiments in Fig. 1, only the first points appear to follow the linear law required by the integrated form of Equation 1, and the curvatures near the end are evidence of some disturbing side reaction, which becomes more important at higher (Br-). (Table I will show the values of k—and hence of k'—from Experiments 3 and 7 to be far too small; the curvatures probably indicate that the decrease in k' becomes relatively more important near the end; if such is the case then k' for these experiments is probably never constant, and its values are not simply related to the specific rate of Reaction 9.)

In order to minimise this complication, subsequent experiments were performed at very low (Br<sup>-</sup>), produced by maintaining (Ag<sup>+</sup>) at the value permitted by the solubility of silver oxalate. (If reaction mixtures containing solid  $Ag_2C_2O_4$  are exposed to light for a long time, photochemical decomposition of this solid may induce complications.) The data for No. 32, Fig. 1, are typical of reaction mixtures containing  $Ag^+$ , so long as  $(a_{H^+})$  is greater than  $I\cdot 4\times IO^{-7}$ ; at lower values a slight curvature appears; for these basic solutions the rate constants in Table I correspond to the values of the initial limiting slopes.

### Discussion of Results.

The rate "constants" in the last column of Table I are defined by the equation

$$k = \frac{k'K_2}{(a_{H^+})(C_2O_4^{--})} = \frac{k'}{(HC_2O_4^{-})}$$
 . (12)

 $(K_2$  is the dissociation constant of  $\mathrm{HC_2O_4}^-$  in concentration units.) In order to obtain them from the k' values, it is necessary first of all to evaluate the  $(\mathrm{HC_2O_4}^-)$  in our reaction mixtures; for this evaluation there is available the activity of hydrogen ion, which is given in the buffer tables,  $^{12}$  but not its concentration. Since the activity coefficients for the various ions in our solutions are not known, no thermodynamically exact method for calculating  $(\mathrm{HC_2O_4}^-)$  is feasible; and this is true whether the use of a dissociation constant involving activities or of one involving concentrations is considered. We have chosen the following method of procedure: Values of  $K_2 = (\mathrm{H^+})(\mathrm{C_2O_4}^-)/(\mathrm{HC_2O_4}^-)$  were obtained at different temperatures and ionic strengths (cf. column 9, Table I) by use of the equation given by Griffith, McKeown and Winn (Ref. 7, p. 122) for potassium salts at  $21.5^\circ$ ; in using this equation, the ionic strength terms were assumed independent of temperature; values of the first term at any temperature were calculated from its value at  $21.5^\circ$  by use of -1300 cal. (Ref. 7, p. 122) for the heat of dissociation of  $\mathrm{HC_2O_4}^-$ . These values of  $K_2$  were then used in the (approximately correct) expression

$$(\mathrm{HC_2O_4^-}) = \frac{(a_{\mathrm{H}^+})(\mathrm{C_2O_4^{--}})}{K_2} = \frac{\gamma_{\mathrm{H}^+}(\mathrm{H}^+)(\mathrm{C_2O_4^{--}})}{K_2} \qquad . \tag{13}$$

in order to give (HC<sub>2</sub>O<sub>4</sub><sup>-</sup>).

Since  $\gamma_{H+}$  for all our solutions is probably less than unity, a value of (HC<sub>2</sub>O<sub>4</sub><sup>-</sup>) calculated in this way is probably too small, in which case the k obtained by use of Equation 12 is too large.

So long as Reaction 9 is the only rate-determining step, the law

$$-\frac{d(HBrO)}{dt} = k_1(HBrO)(HC_2O_4^{-}) . (14)$$

will be obeyed and k will obviously remain identical with  $k_1$ . A systematic departure from constancy of the k values may thus indicate that another rate-determining step has appeared. An examination of the last column in Table I will reveal no such systematic variation in k with changes in either (Br<sup>-</sup>) or (C<sub>2</sub>O<sub>4</sub><sup>--</sup>), or ( $a_{H^+}$ ) at values greater than, say,  $5(10^{-7})$  of the latter; but as  $(a_{\rm H}^+)$  decreases further, k increases

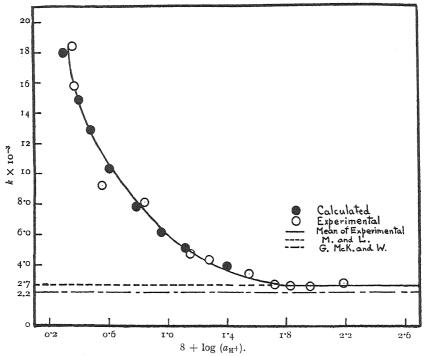


Fig. 2.—Change of k with the activity of hydrogen ion.

quite markedly until for the most basic mixture its value has become over six times the limiting value in acid solution.

In Fig. 2 the k values of Table I have been plotted as ordinate against  $\log (a_{H^+})$ . The upper horizontal line represents the constant value k assumes in acid solution; this limit,  $2.7 \times 10^3$  is our value for  $k_1$  at 0°; the agreement with  $k_1=2.2 \times 10^3$  (at zero ionic strength), obtained by extrapolating the results of Griffith, McKeown and Winn 7 to 0° 13 is entirely satisfactory; it may be mentioned that the small

<sup>13</sup> The value  $k_1=2\cdot 2$  (10<sup>3</sup>) at zero ionic strength was obtained as follows: The values given by Griffith, McKeown and Winn for  $k_1K'$  at three temperatures and  $\mu_c = 0.19$  (Ref. 7, Table VII) were extrapolated to  $0^\circ$ ; to correct to  $\mu_c = 0$  $k_1 \bar{K}'$  at  $\mu_c = 0$ this result was multiplied by the ratio  $\frac{\kappa_1 \Lambda}{k_1 K'}$  at  $\mu_c = 0$  at 21.5° (Ref. 7, Table XII), and divided by the value at 0° of K'. (Jones and Hartmann, Trans. Amer. Electrochem. Soc., 30, 295, 1916, give K' = 5.7 (10<sup>-10</sup>) at 0°). difference which does exist is of the sign and magnitude to be expected from the approximate nature of Equations 12 and 13. The principal object of this investigation thus seems to be accomplished: the value of the specific rate of Reaction 9 is unaffected by the presence or absence of bromine, and the theory of intermediate compounds in halogen reactions has received strong additional support.

The values of k from the solid curve (Fig. 2), which is an average of the experimental points in basic solution, conform to the equation

$$k = k_1 + \frac{\text{const.}}{(a_{\text{H}}+)};$$
 . . . (15)

we suggest, as the simplest explanation of the second term on the right, another rate-determining step, for which the rate is independent of  $(a_{\mathbf{H}^+})$ . Under the conditions of our experiments, this rate could be given by either

$$-\frac{d(\mathrm{HBrO})}{dt} = \kappa \left(\mathrm{HBrO}\right) \left(\mathrm{C_2O_4}^{--}\right) . \qquad . \qquad . \qquad . \qquad . \tag{16}$$

or 
$$-\frac{d(\text{HBrO})}{dt} = k_2(\text{HC}_2\text{O}_4^-)(\text{BrO}^-) = Kk_2\frac{(\text{HBrO})(\text{HC}_2\text{O}_4^-)}{(a_{\text{H}^+})}. \quad (17)$$

(K is the dissociation constant of hypobromous acid.) Such alternative kinetic interpretations of complex rate laws are often possible; <sup>3</sup> they necessitate a choice that must perforce be somewhat arbitrary. The mechanism corresponding to Equation 16 seems unreasonable: for the concentration neither of the hypobromous acid nor of the oxalate ion in a reaction mixture is appreciably altered by changing ( $a_{\rm H}$ +) within the range of Fig. 2, and we should expect a new rate-determining step to involve a substance whose concentration is undergoing marked variation at the conditions under which this new step appears. The value  $K = 10^{-9} \, ^{10}$  for the dissociation constant of HBrO indicates that hypobromite ion is such a substance. This reasoning renders highly probable the rate-determining step

$$BrO^{-} + HC_{9}O_{4}^{-} \rightarrow HCO_{3}^{-} + CO_{9} + Br^{-}$$
 . (10)

as the second in the oxidation of oxalate by bromine (or hypobromous acid). The solid circles in Fig. 2 represent the values of k calculated from  $k_1=2.7\times 10^3$  and  $Kk_2=3.06\times 10^{-4}$ ; if  $10^{-9}$  is the value of K, then the specific rate of Reaction 10 at 0° is  $3\times 10^5$ . The uncertainty in K precludes giving a more accurate value of this specific rate.

Since the experimental results in Fig. 2 conform to the simple Equation 15, we must conclude that (BrO-) is not very large even in slightly basic solution. For, were (BrO-) comparable with (HBrO), the mechanism proposed above would lead to

$$k = \frac{k_1(a_{\rm H^+}) + k_2 K}{(a_{\rm H^+}) + K} \qquad . \qquad . \qquad . \tag{15a}$$

as the expression for k.

It may be ascertained from Fig. 3 that the effect on  $k_1$  of changing the temperature is given by

log 
$$k_1 = \frac{-15700}{4.579} + 16.0$$
; or  $k_1 = 10^{16.0} e^{-\frac{15700}{RT}}$ . (18)

This heat of activation, 15,700 calories, obtained directly from a study of Reaction 9, is to be compared with the value 15,400 calories, given by Griffith, McKeown and Winn. This close agreement has probably resulted from a cancellation of errors somewhere in the calculations involved. A more complete discussion of this point, and of an interpretation of Equation 18 in terms of collisions, will be deferred until the data from our investigation, now almost complete, of the reaction

$$HCIO + HC_2O_4^- = H_2O + 2CO_2 + CI^-$$
 . (19)

are available.

The rate law, Equation 14, has now been established over the entire range of possible oxalate mixtures—chiefly by Griffiths, McKeown,

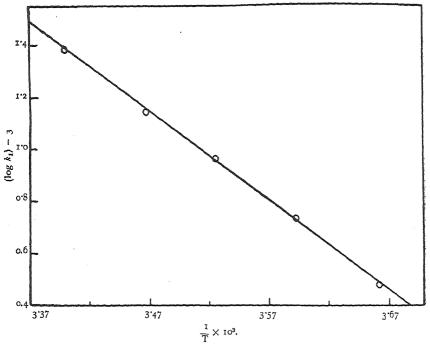


Fig. 3.—Variation of  $k_1$  with the temperature.

and Winn; for at the one extreme in their reaction mixtures, practically all the oxalate was present as  $\mathrm{H_2C_2O_4}$ , while at the other, 90 per cent. of it existed as  $\mathrm{C_2O_4}^{--}$ ; our reaction mixtures complete this series since they contained appreciable oxalate only in the latter form. Now, the only oxalate species not present at infinitesimal concentrations in any of these mixtures is  $\mathrm{HC_2O_4}^{-}$ : therefore, this ion is almost certainly involved in the rate-determining step corresponding to Equation 14; and, consequently, the mechanism (Reaction 9) given by Griffiths, McKeown, and Winn seems established beyond a reasonable doubt. For the sake of completeness, however, we shall point out that, formally, Equation 14 might be interpreted in terms of the mechanism

$$BrO^- + H_2C_2O_4 \rightarrow H_2O + 2CO_2 + Br^-$$
 . (20)

if the proper equilibrium constants were employed. But the Arrhenius constant <sup>14</sup> for this mechanism has a value greater, and probably much greater, <sup>15</sup> than 10<sup>16</sup>; since this number already exceeds by several powers of ten the collision number for a gas reaction (which is approximately 10<sup>13</sup> mols./ell/min. at unit concentration), this mechanism must be discarded as improbable. The reasonableness of the Arrhenius constants corresponding to several mechanisms, all of which are formally permitted by the rate law established for a reaction, may thus serve as a criterion for assigning to this reaction the most reasonable mechanism.

In conclusion we may mention what evidence Table I affords on the question that lead to the investigation of Griffith, McKeown and Winn; namely, the effect of light on Reaction 8. Our experiments show conclusively that Reaction 9, taking place in the absence of bromine, is not photosensitive; any effect of light on Reaction 8 must therefore result either from a change of mechanism (such as an action of bromine atoms) or from a sensitisation of Reaction 9 through light absorption by some substance (such as bromine) not directly involved in the rate-determining step.

### Summary.

1. The rate of the reaction

$$HBrO + HC_2O_4^{-\frac{k_1}{\longrightarrow}} H_2O + 2CO_2 + Br^{-} . . (9)$$

has been measured in the absence of bromine and found to be virtually independent of bromide ion over a large ( $10^{-9}-10^{-6}\,M$ ) concentration range. Our value ( $k_1=2\cdot 7$  ( $10^3$ ) at  $0^\circ$ ) is in close agreement with that deduced by Griffith, McKeown and Winn from the rate law

$$-\frac{d({\rm Br_2})}{dt} = k_1 K' \frac{({\rm Br_2})}{({\rm H^+})({\rm Br^-})} ({\rm HC_2O_4^-})$$

by use of K', the equilibrium constant for the bromine hydrolysis, and this agreement is the most direct evidence yet obtained for the theory that the halogens in aqueous solutions act as oxidising agents only through the hypohalous acids (or their ions). The mechanism of Reaction 9 seems as definitely established as is possible by present kinetic methods.

2. The directly measured value, 15,700 cals., for the (apparent) activation energy of Reaction 9 is also in good agreement with that deduced by Griffith, McKeown and Winn.

3. In basic solution, the overall rate exceeds that of Reaction 9; this increase, which is independent of hydrogen ion, can be satisfactorily accounted for if a second rate-determining step

$$BrO^- + HC_2O_4^- \xrightarrow{k_2} HCO_3^- + CO_2 + Br^-$$
 . (10)

 $^{14}$  The Arrhenius constant is, of course, the intercept at r/T = 0 on the ordinate axis of a graph like Fig. 3; its value, in Equation 18, is 10  $^{16}$ .

15 While accurate data are not available for the calculation of the Arrhenius constant corresponding to Reaction 20, the following approximate value therefor will bear out the conclusion reached above. If at 0° the dissociation constants for oxalic (first stage) and hypobromous acids are 10-1 and 10-9 (footnote 10), the specific rate of Reaction 20 would be 10<sup>3</sup> × 10<sup>-1</sup>/10<sup>-9</sup> = 10<sup>11</sup>; its heat of activation 15700 + 300 - 4000 = 12000 calories, if - 300 cals. is the heat of dissociation for oxalic, and + 4000 cals. that for hypobromous acid. (*I.C.T.*, vol. 5, p. 181.) The Arrhenius constant for a reaction with this specific rate and this activation energy is 10<sup>21</sup>, or 10<sup>8</sup> times the collision number.

is assumed. If the dissociation constant of hypobromous acid has the value  $10^{-9}$  at  $0^{\circ}$ ,  $k_2=3$  ( $10^{5}$ ) at that temperature.

4. In a discussion of possible alternative formulations of these two ratedetermining steps, reasons have been advanced for selecting Reactions 9 and 10 as the corresponding mechanisms.

5. Reaction 9 has been found insensitive to diffuse daylight.

# THE MECHANISM OF THE UPPER LIMIT OF INFLAMMATION OF ELECTROLYTIC GAS MIXTURE.

By N. Semenoff, A. Nalbandjan and F. Dubowizky.

Received 23rd February, 1933.

It is well known that the development of the chain theory is very closely connected with the phenomena of the upper and lower limits of inflammation. The velocity of the chain reaction  $w=\frac{n_0}{1-\alpha}$  can be constant only when  $\alpha<1$ . With  $\alpha\geqslant 1$  the velocity of the chain reaction automatically grows larger and leads to an explosion. In cases of very small  $n_0$  the transition from practically no reaction at all to a very rapid reaction is a very sharp one.  $\alpha$  is a function of the pressure p of the gas mixture. If  $\alpha$  grows with p, reaches a certain maximum and then again diminishes, then we have two pressure limits,  $p_1$  and  $p_2$ , with  $\alpha(p_1)=1$ , and  $\alpha(p_2)=1$ . This means that the velocity of reaction being immeasurably small at  $p< p_1$  and  $p> p_2$  becomes infinitely large at  $p_2>p> p_1$ . That is the theory of the upper and lower limit of inflammation as given by Semenoff 1 and Hinshelwood.2

The first growth of  $\alpha$  with pressure was explained very well by the breaking-up of the chains on the walls of the vessel. The theory of the lower limit was given by Semenoff and proved by several experimenters for different reactions. It was much more difficult to explain the diminution of  $\alpha$  at further pressure growth. Hinshelwood  $^3$  and later Semenoff  $^4$  supposed that this is connected with the breaking-up of the chains in the gas volume. By a certain hypothesis about the mechanism of reaction the probability of the break-up of chains in the gas volume grows at large pressures, and therefore  $\alpha$  diminishes as the pressure increases.

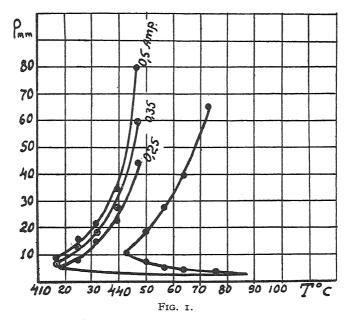
F. Haber and N. Alyea  $^5$  have proved that in the case of the reaction  $H_2+O_2$  the chains begin on the walls of the vessel. But not all kinds of walls can be initial centres of reaction. Aluminium, for instance, is not capable of serving as such, and therefore in aluminium vessels there occurs no inflammation at all of  $H_2+O_2$  at low temperatures.

Haber and Alyea concluded, as is known, from their experiments that the upper limit is not connected with the nature of the gas, but only with the properties of the surface. At pressures corresponding to the upper limits there occur some changes in the gas adsorption on the walls, so that these become incapable of further production of initial

<sup>&</sup>lt;sup>1</sup> Z. physik. Chem., 1B, 192, 1928. 
<sup>2</sup> Proc. Roy. Soc., 122, 1929. 
<sup>3</sup> Ibid., 122, 610, 1929. 
<sup>4</sup> Z. physik. Chem., 6B, 307, 1930. 
<sup>5</sup> Ibid., 193, 10, 1930; Naturwiss., 441, 1930.

centres. In several articles, Hinshelwood 6 argues against such a conclusion, and points out several indirect data which are in contradiction to the point of view of Haber and Alyea, and seem to prove the conception of Hinshelwood and Semenoff.

Haber and Oppenheimer,7 on mixing with oxygen a stream of hydrogen that has been passed over hot tungsten and therefore contains atomic hydrogen, observed inflammation of the mixture at temperatures much lower than that of self-inflammation. But they did not observe in this experiment the phenomenon of the upper limit. It seems, therefore, that this phenomenon vanishes when there is a due number of artificially generated initial centres (in this case hydrogen atoms). This experiment seems to prove the correctness of the theory of Haber and



Alyea. But the last experiments which we made in Leningrad show just the contrary.

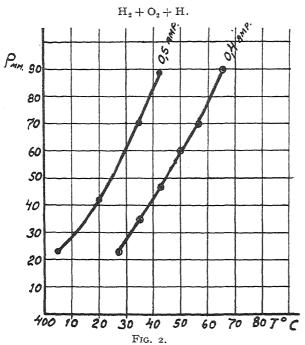
A discharge tube, containing hydrogen at pressures of about 0.4 mm., was heated in a furnace. After passing the discharge through the tube for several seconds (the concentration of H-atoms was about 10-50 per cent.) it was turned off and by a quick turn of the stopcock the mixture. H<sub>2</sub> + O<sub>2</sub>, at a certain pressure, was let in. With this arrangement the region of inflammation of H<sub>2</sub> + O<sub>2</sub> in mixtures containing a constant amount of hydrogen atoms was studied. The results received (see Fig. 1) show that the presence of hydrogen atoms enlarges the region of inflammation but does not change its characteristic form (that of a peninsula). The upper limit remains very sharp, with increase of the current, i.e., with increase of the H-atom concentration the peninsula grows larger, but not very much so. We suppose that the discrepancy of our results with those of Haber and Oppenheimer is connected with the fact that

<sup>&</sup>lt;sup>6</sup> Proc. Roy. Soc., 130A, 670, 1931. <sup>7</sup> Z. physik. Chem., 16B, 773, 1932.

in their experiments the concentration of hydrogen atoms increased with the hydrogen pressure.

In agreement with others we found no self-inflammation when the surface of the discharge tube was covered with aluminium. But in presence of H-atoms there occurred an inflammation, and an upper limit was observed (Fig. 2). This proved that we observed not a surface effect but a volume effect.

We have performed analogous experiments with ions as initial centres. A stream of the mixture H<sub>2</sub> + O<sub>2</sub> passed at first an electrodeless discharge, and then entered a long heated tube. By the stream method



the inflammation region was determined in absence and in presence of the discharge.

We see from Fig. 3 that the inflammation region has become larger, but has conserved its form. The upper limit is sharply. (The curve Ι., the region of selfinflammation, the region II. inflammation in electrical charge.)

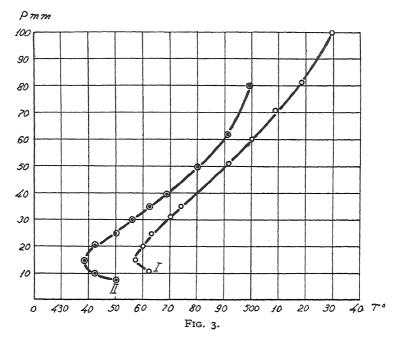
The form of the curve in the case of inflammation condensed spark 8 can be explained

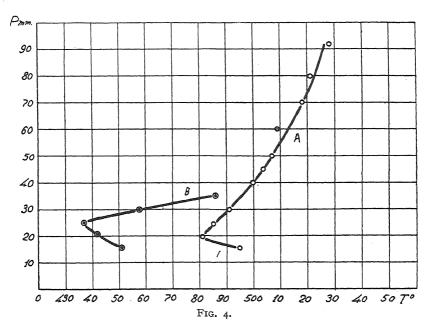
in the same manner as the experiments of Haber and Oppenheimer.9

In the same apparatus, but without a discharge, we performed some further experiments. At a given pressure of the stream we increased the temperature until there occurred an inflammation and a stationary ignition region was obtained. If the ignition took place at low pressures, the flame heated the gas only to a few tens of degrees. This could be determined by calculation as well as directly with a thermo-couple, 10 which was placed in a thin capillary glass tube in the ignition region. While continuing to let the burning stream go we lowered the temperature of the oven. The temperature of the burning region also decreases. At last the flame went out at a certain temperature of the burning region. Using this fact we were able to determine the dependence of the temperature of extinction of the flame upon the pressure. Fig. 4 shows the curve of inflammation (A) and of the extinction (B).

Kowalsky, Z. physik. Chem., 11, 56, 1930.
 Z. physik. Chem., 16, 773, 1932.
 Dubowizky, Physik. Z. Sowjetunion, 1, 586, 1932.

We see that the second curve has a much larger area than the first but is of the same form. The upper limit exists not only for the inflammation, but also for the extinction of the flame.

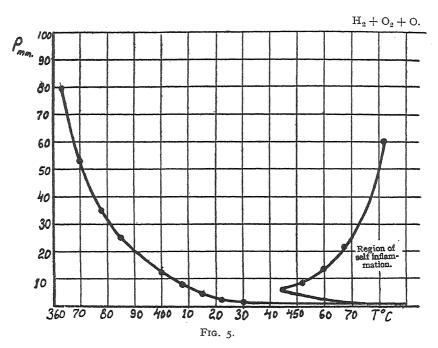




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It seems to us that all these data prove finally the fallacy of the point of view of Hinshelwood and Semenoff. It must be said, however, that the inflammation limits depend in some way upon the number of initial centres. The chain theory of inflammation has to be restricted, namely,  $\alpha$  must itself depend upon the number of active centres. In other words, we must include in the theory the interaction of the chains.  $^{11}$ 

We have now begun experiments on the inflammation of  $\rm H_2 + \rm O_2$  by atomic oxygen. Atomic oxygen seems to act much more strongly than atomic hydrogen. Immeasurably small concentrations of O are enough to lower the inflammation temperature 80-100 degrees. The lower limit, which is very low for high T, increases quickly for T about 420° C. In our experimental arrangement we could not determine the upper limit, but the form itself of the curve (Fig. 5) shows that there



exists an upper limit. Such a strong action of O-atoms seems to prove the validity of the hypothesis first proposed by Semenoff <sup>12</sup> and later by Hinshelwood, <sup>13</sup> that the mechanism of the chain development inside the peninsula of inflammation is

(1) for 
$$H_2 + O_2$$
  $O + H_2 = H_2O^*$   $H_2O^* + O_2 = H_2O + O + O$  (Semenoff);  
(2) for  $CO + O_2$   $O + CO = CO_2^*$   $CO_2^* + O_2 = CO_2 + O + O$  (Semenoff);  
 $O + CO + O_2 = CO_2 + O + O$  (Hinshelwood).

<sup>11</sup> Physikalische Zeitschrift Sowjetunion, No. 4, 1932.

<sup>&</sup>lt;sup>12</sup> Z. physik. Chem., 6, 307, 1930. <sup>13</sup> Proc. Roy. Soc., 138, 297, 1932.

The mechanism proposed by Haber

$$H + O_2 + H_2 = H_2O + OH$$
  
 $OH + H_2 = H_2O + H$ 

seems to be correct only for pressures larger than  $p_2$ , that is the region of stationary chain reactions.

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# THE THERMAL REACTIONS OF PHOSPHOROUS ACID WITH BROMINE AND WITH CHLORINE.

By Robert Owen Griffith and Andrew McKeown.

Received 16th February, 1933.

Most of the reactions of the halogens in aqueous solution apparently fall into two well-defined classes: (a) those in which the reacting entity is the halogen molecule (for example, the reactions of formic acid with bromine and with iodine 1; and (b) those in which the reactant is the hypohalous acid HOX formed by hydrolysis of the halogen (for example, the reaction of iodine with arsenious acid,2 of bromine with hydrogen peroxide,3 and of chlorine, bromine and iodine with oxalates 4). Phosphorous acid is oxidised by chlorine, bromine and iodine in aqueous solution, but only in the last case has the reaction been investigated quantitatively,5 and the mechanism of reaction does not yet appear to be fully elucidated. According to Mitchell, two forms of H<sub>3</sub>PO<sub>3</sub> exist which react simultaneously, the one with the I2 molecule, the other with the I3 ion. It appeared to be of interest to investigate the kinetics of the reactions of phosphorous acid with bromine and with chlorine, with the primary object of discovering in these cases the form in which the halogen enters into reaction, whether as X<sub>2</sub>, or as X<sub>3</sub>, or as HOX.

The bromine, hydrobromic acid and potassium bromide employed were A.R. preparations, while chlorine was prepared from potassium permanganate and hydrochloric acid. The phosphorous acid used contained about 5 per cent.  $\rm H_3PO_4$ , but no appreciable  $\rm H_3PO_2$ . Reaction mixtures were contained in blackened bottles, maintained in thermostats regulated to  $\pm$  0.04°. Samples withdrawn from time to time were discharged into ice-cold acidified KI solution, and the liberated iodine at once titrated against dilute thiosulphate solution.

<sup>&</sup>lt;sup>1</sup> Hammick, Hutchison and Snell, J.C.S., p. 2715, 1925; Hammick and Zvegintzov, *ibid.*, p. 1105, 1926

<sup>&</sup>lt;sup>2</sup> Roebuck, J. physical Chem., 6, 365, 1902; 9, 727, 1905.
<sup>3</sup> Livingston and Bray, J. Amer. Chem. Soc., 45, 1251, 2048; 1923; for further examples cf. also Bray, Chemical Reviews, 10, 161, 1932.

<sup>4</sup> Griffith, McKeown and Winn, Trans. Faraday Soc., 28, 107, 1932; Griffith

and McKeown, *ibid.*, **28**, **518**, **752**, **1932**.

<sup>5</sup> Steele, *J.C.S.*, **93**, 2203, 1908; Mitchell, *ibid.*, **123**, 2241, 1923; Berthoud and Berger, *J. Chim. physique*, **25**, 568, 1928.

Considering first the bromine reaction, preliminary experiments showed that conveniently measurable rates could be obtained only in strong acid solutions; HBr (or  $H_2SO_4$ ) was therefore added to the reaction mixture. The initial concentration of  $H_3PO_3$  has been varied between 0.0108 and 0.3604M, that of Br<sub>2</sub> between M/50 and M/500, and that of HBr between 0.056 and 1.8M. To determine the separate effect of  $[H^+]$  on the rate of reaction experiments were made in which, by addition of KBr, the ionic strength  $(\mu)$  was maintained constant, but the ratio [HBr]/[KBr] was varied. Most of the data were obtained at 10° C.; a few, however, at 20°.

The experiments summarised in Table I. furnish information in respect of all pertinent variables other than temperature, hydrogen ion concentration, and ionic strength on the velocity of the reaction

$$H_3PO_3 + Br_2 + H_2O \rightarrow H_3PO_4 + 2HBr.$$

They show that the velocity is proportional (a) to  $\Sigma \mathrm{Br_2}$ , (b) to  $\Sigma \mathrm{H_3PO_3}$ , and (c) to  $\frac{\mathrm{I}}{K_3 + [\mathrm{Br}^-]}$ , where  $K_3 = \frac{[\mathrm{Br_2}][\mathrm{Br}^-]}{\mathrm{Br_3}^-}$  is the constant of tribromide formation. Columns (2) to (5) give the initial concentrations of the reactants, of HBr (or  $\mathrm{H_2SO_4}$ ), and of KBr. The last column gives the initial values of the unimolecular constant (uni with respect to bromine); these for the present enable true comparisons of specific rate to be made.

Expt.	ΣBr <sub>2(init.)</sub>	ΣH <sub>3</sub> PO <sub>3(init.)</sub>	[HBr].	[KBr].	k <sub>uni</sub> × 10 <sup>2</sup> (init.)
1 2 3	M/50 M/120 M/500	0.0901 0.0001 0.0001	0·8946 0·8946 0·8946		0·844 0·838 0·846
4 5 6	M/500 M/500 M/500	0.0108	0.8946 0.8946 0.8946 [H <sub>2</sub> SO <sub>4</sub> ]		1.66 0.170 0.0104
7 8 9 10	M/500 M/500 M/500 M/500	0.0108 0.0108 0.0108 0.0108	0·73 0·73 0·73 0·73	0·1 0·05 0·025	0·902 1·38 1·86 2·82

TABLE I.—Reaction between  $H_3PO_3$  and  $Br_2$  ( $t = 10^{\circ}$ ).

It will be seen that over a sixteen-fold variation of  $\Sigma H_3 PO_{3(init.)}$  and a ten-fold variation of  $\Sigma Br_{2(init.)}$ , the order of reaction with respect to each of the reactants is unity. An order of reaction of unity with respect to bromine is also indicated by the slow fall with time of the unimolecular constant in each experiment, this fall being quantitatively accounted for by the concomitant fall in  $[H_3PO_3]$  and rise of  $[H^+]$  and of  $[Br^-]$  as the reaction proceeds. A number of experiments (not tabulated) have been carried out with constant [HBr] and varying [KBr], which showed that the rate of reaction is practically inversely proportional to the bromide ion content; but in such comparisons the ionic strength of the reaction mixture was not constant, and, moreover, the total bromide ion concentration was necessarily high, so that it is impossible from them to distinguish between a retardation proportional to  $[Br^-]$  and one proportional to  $K_3 + [Br^-]$ . Experiments 7-10 were

accordingly designed to test the form of the retarding function. In these experiments, the rate of reaction is made conveniently measurable by addition of 0.73M  $H_2SO_4$ , and [KBr] is reduced so as to be comparable with  $K_3$  (which is known to have a value of about 0.05). It will be seen that the rate is not inversely proportional to [Br], since, for example, changing [KBr] from 0.1 to 0.025 only doubles the velocity constant. If, however, the reciprocal of  $k_{\rm uni}$  be plotted against [Br] for the four experiments a straight line results, showing that

$$\frac{1}{k_{\text{uni}}} \propto [\text{Br}^-] + \text{const.}$$

The value of the constant, which is the intercept of the plot on the  $[Br^-]$  axis, is found to be 0.046  $\pm$  0.02, and this is sufficiently close to the value of  $K_3$  to justify the conclusion that  $k_{\rm uni}$  is proportional to  $\frac{1}{K_3 + [Br^-]}$ . Since the concentration of free bromine  $[Br_2]$  is given by  $\Sigma Br_2 \cdot \frac{K_3}{K_3 + [Br^-]}$ , the form of the retardation function shows that only the free bromine is reacting with the phosphorous acid. The possibility of the reactant being HOBr is ruled out, since this would involve a greater retardation by  $Br^-$ , vis., rate  $\infty \frac{1}{[Br^-]\{K_3 + [Br^-]\}}$ . Finally, an experiment (not given in Table I.) in which  $H_3PO_4(0.02M)$  was added to the reaction mixture (containing 0.90M HBr) showed that this resultant has no effect on the rate.

The remainder of the experiments show the effect of  $H^+$ , of ionic strength  $(\mu)$  and of temperature on the velocity. They fall into six series, in each of which the sum [HBr] + [KBr] is maintained constant, and  $[H^+]$  varied by altering the ratio [HBr]/[KBr]. The ionic strength (effectively the sum of [HBr] and [KBr]) has been varied between 1.8 and 0.225. Five of the series relate to a temperature of 10°; the sixth to 20°. Table II. presents the data. In view of the conclusions drawn above, we may express the rate of reaction by the equation

$$\frac{dx}{dt} = k \cdot \frac{\Sigma Br_2 \times \Sigma H_3 PO_3}{K_3 + [Br^-]}.$$

The velocity coefficients k given in the third column of Table II. have been evaluated on this basis, initial values being taken where necessary. Inspection of the data for each series shows that k falls markedly with increasing  $[H^+]$ , but that the relationship between k and  $[H^+]$  is not a simple one. If the free bromine were reacting with  $H_3PO_3$  molecules, or  $H_2PO_3^-$  ions, or  $HPO_3^-$  ions, the rate of reaction, under our experimental conditions, should approximately be independent of  $[H^+]$ , or inversely proportional to  $[H^+]$ , or inversely proportional to  $[H^+]$  respectively. Actually the relationship lies between the last two alternatives, which suggests that the measured reaction is composite of two independent processes, represented by

(1) 
$$\mathrm{Br_2} + \mathrm{H_2PO_3}^- + \mathrm{H_2O} \rightarrow \mathrm{H_2PO_4}^- + 2\mathrm{Br}^- + 2\mathrm{H}^+ \dots k_1$$
  
(2)  $\mathrm{Br_2} + \mathrm{HPO_3}^- + \mathrm{H_2O} \rightarrow \mathrm{HPO_4}^- + 2\mathrm{Br}^- + 2\mathrm{H}^+ \dots k_2$ 

<sup>6</sup> Griffith, McKeown and Winn, Trans. Faraday Soc., 28, 101, 1932.

TABLE II.—Reaction between  $H_3PO_3$  and  $Br_2$ .

[HBr].	[H+].	k.	$k\{K_1+[{ m H}^+]\}.$	[HBr].	[H <sup>+</sup> ].	k.	$k\{K_1+[H^+]\}.$
$\mu = 0.0745$ 0.1118 0.2236  Series B, $\mu = 0.1129$ 0.2258 0.4517  Series C,	[HBr] + [	KBr] = 0 2.643 1.537 0.589 ; £H <sub>3</sub> PO <sub>5</sub> (KBr] = 0 1.855 0.706 0.259 ; £H <sub>3</sub> PO <sub>5</sub>	0·4695 0·3295 0·1918 =0·0108; 0·4517. 0·4045 0·2325 0·1435 =0·0108;	$\mu = [F]$ 0.1129 0.1694 0.2258 0.4517 0.9035  Series D, $\mu = [D]$ 0.1355 0.3610 1.355  Series E,	HBr] + [F   0.1179     0.1734   0.2291   0.4537   0.9045     t=10°. C.   HBr] + [   0.1526   0.370   1.358	(SBr] = 0.4.483 2.510 1.671 0.616 0.235 ; ΣH <sub>3</sub> PO (KBr] = 1 (1.258 0.325 (0.0492 ; ΣH <sub>3</sub> PO	0.9770 0.6864 0.5500 0.3410 0.2360 3=0.0432; 355. 0.3177 0.1529 0.0718 3=0.0901;

On this basis, the reaction rate is given by

$$\begin{split} \frac{dx}{dt} &= k \cdot \frac{\varSigma \text{Br}_2 \times \varSigma \text{H}_3 \text{PO}_3}{K_3 + [\text{Br}^-]} = k_1 [\text{Br}_2] [\text{H}_2 \text{PO}_3^-] + k_2 [\text{Br}_2] [\text{HPO}_3^-]. \\ \text{But} \\ [\text{H}_2 \text{PO}_3^-] &= \varSigma \text{H}_3 \text{PO}_3 \cdot \frac{K_1}{K_1 + [\text{H}^+]}, \quad [\text{HPO}_3^-] = \varSigma \text{H}_3 \text{PO}_3 \cdot \frac{K_1 K_2}{[\text{H}^+] \{K_1 + [\text{H}^+]\}'} \\ \text{and} \quad [\text{Br}_2] &= \varSigma \text{Br}_2 \cdot \frac{K_3}{K_3 + [\text{Br}^-]}, \quad \text{where} \quad K_1 \quad \text{and} \quad K_2 \quad \text{are the first and} \end{split}$$

second ionisation constants of H<sub>3</sub>PO<sub>3</sub>. Hence

$$k = \frac{k_1 K_1 K_3}{K_1 + [\mathbf{H}^+]} + \frac{k_2 K_1 K_2 K_3}{[\mathbf{H}^+] \{K_1 + [\mathbf{H}^+]\}},$$

or

$$k\{K_1+[\mathcal{H}^+]\}=k_1K_1K_3+\frac{k_2K_1K_2K_3}{[\mathcal{H}^+]}.$$

Owing to various difficulties, it is not possible to make a completely satisfactory test of this mechanism, though the approximation method outlined below at least demonstrates its plausibility. The only certain method of testing it would be to isolate one of the part-processes and to study the influence of all variables on the rate of this process. This, however, is not feasible, since the necessary drastic alterations of experimental conditions would preclude the accurate measurement of reaction velocity. Any other method must necessarily involve assumptions regarding (a) the dependence of  $K_1$  on ionic strength and (b) the dependence of all the constants  $k_1$ ,  $k_2$ ,  $K_1$ ,  $K_2$  and  $K_3$  on the ratio [HBr]/[KBr] at constant ionic strength. Considering (b) we shall assume

that each of the constants  $k_1$ ,  $k_2$ ,  $K_1$ ,  $K_2$  and  $K_3$  is independent of the ratio [HBr]/[KBr] with  $\mu$  constant. This assumption can only be roughly true, since it is known that  $K_3$  is somewhat greater in KBr than in HBr of the same strength.<sup>6</sup> The difference is, however, small—about 4 per cent. for solutions of ionic strength greater than 0.3; it seems probable that none of the other constants mentioned varies to a greater extent. We shall therefore write for each series (constant  $\mu$ ):

$$k_1K_1K_3 = k'$$
, and  $k_2K_1K_2K_3 = k''$ ,

where k' and k'' are constants for each series.

Hence 
$$k\{K_1 + [H^+]\} = k' + \frac{k''}{[H^+]}$$
.

The plot of  $k\{K_1+[H^+]\}$  against  $I/[H^+]$  at constant  $\mu$  should thus be a straight line, the slope giving the value of k'' and the intercept on the  $k\{K_1+[H^+]\}$  axis the value of k'. To enable these plots to be made, however, information is required with regard to the value of  $K_1$  and its dependence on  $\mu$ . The first ionisation constant  $(K_1)$  of phosphorous acid has been determined by Kolthoff, who finds by the conductivity method that it increases from 0.016 to 0.062 as the concentration of  $H_3PO_3$  increases from 0.001 to 0.1M., i.e. as  $\mu$  increases from 0.001 to 0.05. The range of  $\mu$  we are concerned with is higher, viz. from 0.2 to 1.8; from analogy with the variation with  $\mu$  of the first ionisation constant of oxalic acid (cf. Dawson, Hoskins and Smith ), an acid of very nearly the same strength as  $H_3PO_3$ , we should anticipate that  $K_1$  goes through a very flat maximum in the above range of  $\mu$  with  $K_1$  (max.) of the order of 0.1. We have therefore used the value  $K_1 = 0.1$  to calculate  $[H^+]$  and  $K_1 + [H^+]$ , assuming it to be independent of  $\mu$ .

The resulting plots are shown in Fig. I, and are in each case linear within the experimental error. It may be pointed out that for series C, C' and E, the last experiments of each series fall on straight lines using any reasonable value of  $K_1$ ; in order that the points corresponding to the first one or two experiments of the series (experiments with low  $[H^+]$ ) should also lie on the straight line, the value  $K_1=0.1$  must be used, as also is the case for all the experiments in series A and B, where necessarily all the data refer to low values of  $[H^+]$ . It seems hardly possible that for all the series these linear relations are accidental and caused by compensating variations in the various constants; it would appear much more likely that in the range of  $\mu$  employed  $K_1$  is approximately constant at the value 0.1, and that, moreover, the variations in the products  $k_1K_1K_3$  and  $k_2K_1K_2K_3$  at constant  $\mu$  but changing ratio [HBr]/[KBr] are not serious.

We shall therefore base our calculations on these assumptions. The values of k' and k'' then obtained from the plots of Fig. 1 are given in Table III. The Table shows that both k' and k'' go through maxima with increasing  $\mu$ . Since  $k' = k_1 K_1 K_3$  and  $k'' = k_2 K_1 K_2 K_3$ , we may proceed to calculate approximate values of the velocity coefficients of reactions (1) and (2) by use of the following values:  $K_1 = 0.1$  at both 10° and 20°,  $K_2 = 2 \times 10^{-7}$  at 10° and 20° (Nylen, 9 Kolthoff 7) and

9 Nylen, Diss., Upsala, 1930.

<sup>&</sup>lt;sup>7</sup> Kolthoff, Rec. trav. Chim., 46, 350, 1927.

<sup>8</sup> Dawson, Hoskins, and Smith, J.C.S., p. 1884, 1929.

Series.	t° C.	μ.	k'.	k".
A B C D E C'	10 10 10 10 10	0·2236 0·4517 0·9035 1·355 1·789 0·9035	0.0460 0.0513 0.0465 0.0398 0.0332 0.128	0.0329 0.0416 0.0443 0.0424 0.0351 0.097

TABLE III.-REACTION BETWEEN H3PO3 AND Br2.

 $K_3 = 0.046$  at 10° and 0.0505 at 20°. For the series C and C' ( $\mu = 0.9035$ ) we then obtain:

$$k_1 = 10.1$$
 at 10° and 25.3 at 20°,  
 $k_2 = 4.8 \times 10^7$  at 10° and 9.6 × 10<sup>7</sup> at 20°,

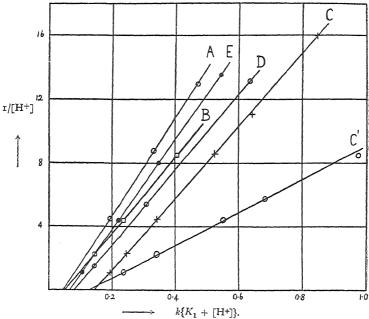


Fig. 1.—For D and E both scales doubled. For C ordinate axis displaced on unit, to the right.

both constants being in the units  $\frac{\text{litres}}{\text{moles-min}}$ . The temperature coefficients of  $k_1$  and  $k_2$  are thus 2.5 and 2.0 respectively, corresponding to critical increments of 15100 cal. and 11400 cal. The absolute value of  $k_2$  (reaction between  $\text{Br}_2$  and  $\text{HPO}_3^{--}$  ions) is a high one.

It is to be noted that experiments 7-10 of Table I, from which the dependence of rate on [Br] was obtained, relate to conditions such that the two part-processes are contributing approximately equal shares to the observed rate; the conclusion that rate is proportional to  $\frac{I}{K_3 + [Br]}$ , therefore holds for both part-processes. In addition to the experiments

summarised in Table II, a few experiments have been made with (1) KCl and (2) NaBr as the neutral salt. Thus, in an experiment identical with the fifth of series C except that KCl was substituted for KBr, the constant k obtained was 0.244 instead of 0.268. The small decrease may be due to reduction in the concentration of free bromine owing to slight complex formation between Br<sub>2</sub> and Cl<sup>-</sup> (Br<sub>2</sub> + Cl<sup>-</sup>  $\rightleftharpoons$  Br<sub>2</sub>Cl<sup>-</sup>). On the other hand, when NaBr is substituted for KBr slightly higher velocities are obtained, as shown by comparison of the second and fourth experiments of series C with the two experiments given below.

$$t = 10^{\circ}$$
;  $\Sigma H_3 PO_3 = 0.0108$ ;  $\mu = [HBr] + [NaBr] = 0.9035$ .

[HBr].	[H <sup>+</sup> ].	k.	$k\{K_1 + [H^+]\}.$
0.0847	0.0904	2.98	o·568
0.2258	0.2291	0.746	0.246

This difference is probably due to  $K_3$  being greater in NaBr solutions than in KBr solutions,<sup>6</sup> but the possibility is not excluded that the other constants  $(k_1, k_2, K_1, K_2)$  are also somewhat different.

The reaction between phosphorous acid and chlorine has also been studied at a temperature of 10° C., precautions being taken to avoid loss of chlorine by volatilisation (cf. Griffith and McKeown 4). Preliminary experiments showed the reaction to be unimolecular with respect to each reactant, and hence in Table IV, which summarises the main experiments, the velocity constants ( $h_{\rm bi}$ ) given are bimolecular constants defined by the equation

$$\frac{dx}{dt} = k_{\rm bi} \cdot \Sigma {\rm Cl_2} \times \Sigma {\rm H_3 PO_3},$$

the units being  $\frac{\text{litres}}{\text{moles-min}}$ .

TABLE IV.—Reaction between  $H_3PO_3$  and  $Cl_2$  ( $t = 10^{\circ}$  C.).

					-	-		
$_{k_{ m bi}}^{ m [HCl]}$		:	0·01265 3·40	0·2025 2·29	o·253 1·936	o·506 o·930	1·012 0·3924	
[HCl] [NaCl] k <sub>bi</sub>	:	:	o·1265 o·8855 4·73	0·2025 0·813 2·63	0·253 0·762 2·075	0·354 0·661 1·402	0·506 0·508 0·9145	1·012 — 0·3924
[HCl] [KCl]	:	:	0·263 0·749	0·512 0·500				

These results show that, as in the  $\mathrm{Br_2}-\mathrm{H_3PO_3}$  reaction, the reactant is the free halogen. The velocity should then be inversely proportional to  $K_3+[\mathrm{Cl}^-]$ ; since, however,  $K_3$  (the constant of trichloride formation) has the value of approximately 5·0, 10 the velocity should not be markedly dependent on [Cl-], which agrees with the experimental findings. Further, the retardation by [H+] is of a similar nature to that found in the  $\mathrm{H_3PO_3}-\mathrm{Br_2}$  reaction, i.e. it lies intermediate between a retardation proportional to  $K_1+[\mathrm{H}^+]$  and one proportional to

<sup>10</sup> Sherrill and Izard, J. Amer. Chem. Soc., 53, 1667, 1931.

 $H^+]\{K_1+[H^+]\}$ . A similar mechanism may therefore be presumed. On attempting, however, to interpret the results of Table IV on this basis, the plots of  $k_{bl}\{K_3+[Cl^-]\}$ .  $\{K_1+[H^+]\}$  against  $I/[H^+]$  are not linear, but slightly concave to the  $I/[H^+]$  axis; it is therefore not possible to evaluate the separate contributions to the observed rate of the two presumed part-processes:—

$$Cl_2 + H_2PO_3^- + H_2O \xrightarrow{k_1} H_2PO_4^- + 2H^+ + 2Cl^-$$
  
 $Cl_2 + HPO_3^{--} + H_2O \xrightarrow{k_2} HPO_4^{--} + 2H^+ + 2Cl^-$ 

If the mechanism is correct, the non-linearity of the plots above-mentioned is due to considerable variations in one or more of the constants  $k_1$ ,  $k_2$ ,  $K_1$ ,  $K_2$  and  $K_3$  in HCl-NaCl mixtures of constant  $\mu$  and varying ratio [HCl]/[NaCl]; it is therefore not at present possible to elucidate the kinetics further.

### Summary.

The kinetics of the reactions of phosphorous acid with bromine and with chlorine have been investigated, the former reaction in presence of HBr (or H<sub>2</sub>SO<sub>4</sub>) and neutral bromides, and the latter reaction in HCl and neutral chlorides. Each reaction is found to be bimolecular, but retarded by hydrogen ion and the halide ion resulting. The data are interpreted in terms of two simultaneous processes of the type

$$X_2 + H_2PO_3^- + H_2O \rightarrow H_2PO_4^- + 2HX$$
  
 $X_2 + HPO_3^- + H_2O \rightarrow HPO_4^- + 2HX$ ,

where X2 is the free halogen molecule.

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# STUDIES IN OPTICAL ACTIVITY, PART II. A NEW TYPE OF POLARIMETER.

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There are two distinct methods of measuring the variation of optical rotatory power with wave-length in the visible spectrum. Either monochromatic sources of light are used and the polarimeter settings made visually, or a line spectrum is projected through the polarimeter on to the slit of an auxiliary spectrograph, and comparison of the double or triple fields made after development of the photographic image. A review of the different kinds of instrument available was contributed by Descamps <sup>1</sup> to the recent General Discussion of the Faraday Society on Optical Rotatory Power.

A polarimeter was required here for the investigation of optically active co-ordination compounds. These substances usually possess two well-defined absorption bands in the visible and near ultra-violet spectrum.

<sup>&</sup>lt;sup>1</sup> Trans. Far. Soc., 26, 357, 1930.

One or other, or both, of the bands effectively control the rotatory dispersion, and it is therefore necessary for quantitative studies to make measurements of rotatory power within the regions of absorption. The deeply-coloured solutions greatly reduce the light intensity, which in any case is small after passing through a polarimeter adjusted for "minimum illumination," and attempts to counteract this by increasing the halfshadow angle result in loss of accuracy. Monochromatic sources of light sufficiently powerful for ordinary polarimetric work are few in number,2 and even if it were possible to make use of some of them in the present undertaking, the points thus gained would be of little value on account of the anomalous character of curves of rotatory dispersion in the neighbourhood of "active" absorption bands. The photographic method has obvious advantages, but must entail long exposures, and this raises another difficulty. Many optically active complex salts undergo fairly rapid racemisation in aqueous solution, and consequently long exposures are out of the question. It was therefore doubtful whether the standard types of polarimeters would meet the requirements of the research, and it became necessary to devise one.

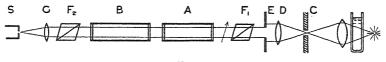


Fig. 1.

The essential features of the new instrument are as follows. Nicol prisms are set at some distance apart along a common axis with their principal planes inclined at an angle  $\theta$  ( $\theta = 55^{\circ}$ ). A parallel beam of white light sent through both prisms suffers considerable loss of intensity (proportional to  $\cos^2 \theta$ ) in passage and is brought to a focus upon the slit of a direct vision spectrometer. The optical path is illustrated, purely diagrammatically, in Fig. 1. If a polarimeter tube A, containing cane sugar solution of appropriate concentration is interposed, a narrow black band is observed at some part of the spectrum. This is the result of "crossing" the Nicol prisms by superposition of the rotation of the second Nicol and of the cane sugar at the wave-lengths in question. The narrowness of the band is dependent upon the variation with wavelength of the rotatory power of cane sugar. The application of the instrument is based upon the fact that interposition of a second tube of an optically active liquid at B causes a measurable displacement of the position of extinction.

### Calibration.

The rotation dispersion of a solution of cane sugar made by dissolving 26 gms. of specially purified sugar in 100 c.c. of aqueous solution has been accurately determined by Lowry and Richards.<sup>3</sup> This will be referred to hereafter as "standard sugar solution." Measurements made here with the British Drug Houses' "A. R. Sucrose" have been found to check their figures at the wave-lengths 5893, 5461, and 4359 Å within the limits of accuracy allowed by our Schmidt and Haensch polarimeter. Moreover, it has been ascertained that a 10 per cent. variation of concentration in either direction makes no appreciable difference to the molecular rotation of cane sugar.<sup>4</sup> By making use of polarimeter tubes of

<sup>&</sup>lt;sup>2</sup> Lowry, J.C.S., 103, 1062, 1913. 
<sup>3</sup> J.C.S., 125, 2511, 1924. 
<sup>4</sup> I am indebted to Mr. A. Mead, B.Sc., for these measurements.

different lengths and sugar solutions of concentrations varying between about 23 and 29 gms. in 100 c.c., it is possible to record positions of extinction at numerous points in the visible spectrum from 4300 Å to to 6800 Å. Since the rotation is directly proportional to the length of the tube and the concentration of the sugar, each individual result may be expressed as equivalent to that produced by a calculated length of sugar solution of the standard strength. The equivalent tube lengths are plotted against the corresponding extinction points (in Ångstrom units) on a large scale graph. This is the Calibration Curve. Points were actually obtained at intervals of about 60 Å throughout the spectrum, and were found to lie upon a smooth curve.

In order to determine the rotatory dispersion of an optically active substance, a tube containing sugar solution (not necessarily of known strength) is placed between the Nicol prisms, and the position of the dark band located. A second tube containing a solution of which the rotation is required is then placed in front of the first, and the new extinction point is ascertained. By reference to the Calibration Curve both these readings of wave-length may be translated into equivalent lengths of standard sugar solution, and the difference between them is a length of standard solution having a rotation equal to that of the optically active substance at the second wave-length. From Lowry and Richard's rotation-dispersion formula the actual rotation of the substance at that wavelength can be calculated. Any number of points can be obtained in this fashion.

### Details of Construction.

The source of light was a carbon arc, operating automatically on a current of about 16 amperes. A powerful steady source of continuous radiation is essential. The radiation from the arc was filtered through 12 cms. of water (to remove the greater part of the radiant heat), collected by a lens of large aperture and brought to a focus at the centre of a small circular hole in a large screen, C (Fig. 1), which effectively shielded the observer from stray light. The beam was collimated by the lens D, placed at its focal distance from C, and reduced to a diameter of about

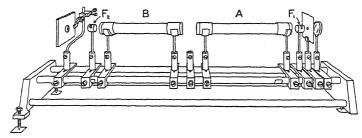


Fig. 2.—Polarimeter.

0.9 cm. by the orifice in the small screen E. Reference should now be made to Fig. 2.

Two Foucault prisms,  $F_1$  and  $F_2$ , 80 cms. apart, have been used in place of Nicol prisms, because it is hoped to extend the application of the instrument to the ultra-violet spectrum. Each of the prisms could be rotated about the common axis and be clamped in any position. The hollow cylinders A and B were of brass, 11 ins. and 14 ins. long respectively (in Fig. 2 the relative lengths have been accidently inverted) and

accurately drilled to carry polarimeter tubes. It is obviously essential that the polarimeter tubes should be exactly and rigidly aligned. The ends of the cylinders were closed with tightly-fitting ebonite caps, having circular orifices to permit the passage of the beam of light. For convenience of manipulation the brass cylinders merely rested in rigid semi-circular supports; were removed for the purpose of introducing the polarimeter tubes and afterwards replaced. The lens G was mounted in such a way as to be capable of slight adjustment by hand. The spectrometer S was the well-known constant deviation model DI, of Adam Hilger. The needle-pointer in the eye-piece was replaced by a very fine vertical hair of glass which extended right across the spectral image. In taking a reading of extinction, the wave-length drum was rotated until the hair-line bisected the dark band. The wave-length drum was calibrated throughout its entire length against some hundred lines in the spectra of H, He, Ne, Hg, Fe, Cu, and W, and a set was made periodically upon the D line of sodium to check the adjustment of the prism. A spectrometer possessing a higher dispersion at the red end of the scale would be a decided improvement.

### Discussion of the Method.

Cane sugar is an ideal substance for use in this instrument, being easily and cheaply obtained in a high state of purity. It is very soluble in water, transparent to visible and near ultra-violet radiation, and the mol-rotation is remarkably insensitive to changes of concentration and temperature. The aqueous solutions deteriorate in time and become cloudy, but fresh lots can be quickly prepared.

Five polarimeter tubes, 25, 20-5, 17, 14, and 11-5 cms. long were supplied by Messrs. Bellingham and Stanley, the requisite lengths being calculated on the assumption of  $\theta=55^{\circ}$ , for use with sugar solutions of concentrations in the neighbourhood of 26 gms. in 100 c.c. Unless it is desired to measure the rotation of a substance within 20 Å or so of a specific wave-length, it is not necessary to know the strength of the sugar solution used, once the Calibration Curve has been obtained. Small variations in room temperature do not appreciably affect the results, but temperature gradients inside the tubes of sugar solution cause large errors, and it is therefore advisable to leave them in the polarimeter room for at least half an hour before use.

It was at first intended to invent a polarimeter tube of adjustable length in which a single sugar solution of the standard concentration could be used, but the design presented many difficulties and the idea was abandoned. An instrument might be constructed on the lines of a Babinet Compensator, the sliding wedges being of dextro or lævorotatory quartz with the optical axis in each wedge at right angles to the incident face.

The method is by no means as simple as it appears superficially, and its accuracy can only be judged by comparison of results with those obtained, using polarimeters of proved reliability. When the rotatory dispersion is anomalous, inaccuracies may conceivably arise on account of unsymmetrical broadening of the dark band due to peculiarities in the summation of the super-imposed rotations. The error should be slight if the anomalous region extends over a wide range of wave-lengths, as in the case of optically active potassium cobaltioxalate (Part III), where the maximum and minimum on the curve of rotatory dispersion are separated by nearly 800 Å.

The smaller the angle between the principal planes of the Foucault prisms, the larger is the number of sugar molecules which must be placed in the path of the polarised ray, in order, effectively, to "cross" the prisms, and consequently the greater the variation of rotatory power with wave-length. This condition produces a narrow dark band, of which the mid-point can be accurately located. On the other hand, a large rotation-dispersion implies a relatively small displacement of the extinction point produced by the super-imposed rotation of the substance under test; that is,  $\frac{\Delta \lambda}{\Delta \sigma}$  is small because  $\frac{\Delta \sigma}{\Delta \lambda}$  is large,  $\sigma$  representing the rotation and  $\lambda$  the wave-length. It is therefore necessary to compromise between working with a narrow dark band and low sensitivity, and a wide band with high sensitivity. An angle of about 55° between the

wide band with high sensitivity. An angle of about 55 between the principal planes of the Foucault prisms was chosen, with special regard to the fact that the object in view was the examination of highly absorbing solutions. But it is unnecessary to know the precise value of the

angle  $\theta$ .

Factors controlling the apparent width and sharpness of the dark band are the following. The intensity of the beam of light, the distribution of energy amongst the various wave-lengths; the dispersive power of the prism; the angle,  $\theta$ , between the principal planes of the Foucault prisms, the rotation-dispersion of the sugar solution, the absorptive power of the coloured solution, and the sensitivity of the eye. Each spectral region possesses special characteristics in respect of the variables. As already emphasised,  $\theta$  cannot be diminished indefinitely without loss of sensitivity. Furthermore, the reproducibility of readings depends upon the effect of slight movements of the wave-length drum of the spectrometer. At the red end of the spectrum the small dispersion of the prism causes the dark band to appear very narrow, but this is offset by the susceptibility of the wave-length reading to small rotations of the drum. In the blue the inconvenience of a broader band of extinction is compensated by the much wider spacing of the graduation marks on the drum.

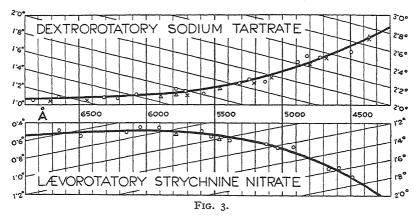
In bringing the hair-line upon the mid-point of the dark band, the assumption is made that the boundaries represent equal angular displacements of the Foucault planes from the exact extinction point (that is, equal amounts of uncrossing of the prisms), a circumstance which arises from the inability of the eye to detect very small intensities of light. Obviously, the correctness of this assumption is conditioned by the interplay of the various factors enumerated above, chief of which is the dispersive power of the prism. The error is certainly slight, and is probably eliminated by the method used in obtaining readings. All actual measurements of rotation depend upon the detection of small changes in the position of extinction. Therefore, an error committed in the first reading is likely to be repeated in the second, and disappears on taking the difference. The difference determines the magnitude of rotation. A trifling error made in locating the optical centre of the dark band in the second reading results in the rotation being assigned at not quite the correct wave-length, but a mistake here of two or three Angstrom units is not significant.

### Application.

Colourless Solutions.—In order to make sure that the method was free from systematic errors, the examination of two colourless,

optically active substances was first undertaken. Neutral sodium tartrate and strychnine nitrate were selected. Aqueous solutions of the tartrate have been studied by Lowry and Austin, but no rotation-dispersion data for the mineral salts of strychnine seem to be available. It was thought desirable to arrange that the rotations were of the same order of magnitude as those expected from coloured complex salts. The observed rotations are plotted against wave-length in Fig. 3. The circles are points recorded by the instrument, the triangles by the Schmidt-Haensch polarimeter with monochromatic illumination, and the crosses are derived from Lowry and Austin's data for sodium tartrate. All things considered, the general agreement is as good as can be expected. On the average, the points lie off the curves by about 3 per cent. of the actual rotations. No systematic errors are indicated, nor does one spectral region seem to be favoured more than another. Of course, had it been intended to study colourless compounds exclusively, the angle  $\theta$ could have been increased with appreciable gain in accuracy.

Coloured Solutions.—No coloured optically active compound exists of which the anomalous rotatory dispersion is known with sufficient



accuracy to permit of testing with it the behaviour of the new polarimeter. Since, however, the instrument has given satisfaction in the case of colourless solutions, the further extension seems justified, with the reservations already made in a previous section. Reference to Part III of this series of papers shows that the degree of reproducibility of individual points established for sodium tartrate and strychnine nitrate is not much lessened in application to the coloured solution of potassium cobaltioxalate,  $K_3[Co(C_2O_4)_3]$ . It is desirable to ascertain how the new polarimeter compares with the standard models in measurements of anomalous rotatory dispersion, for the accuracy of ordinary polarimeters is much impaired by use with coloured solutions. Owing to the lack of experimental data, however, it is surprisingly difficult to form an estimate of the accuracy with which measurements of anomalous rotatory dispersion have been made. The recent publications of Werner Kuhn furnish numerous examples of anomalous rotatory dispersion in the ultra-violet, but in no instance are the actual measurements placed on Jaeger 6 and his collaborators employed a Schmidt and Haensch

<sup>&</sup>lt;sup>5</sup> Phil. Trans., 222A, 249, 1922.

polarimeter of the Lippich pattern and the dispersed light from a Nernst lamp. They were unable to make reliable measurements on potassium cobaltioxalate 7; in the case of potassium chromioxalate an entirely erroneous conclusion as to the relative magnitudes of the rotations obtained with the green and yellow lines of the mercury arc would be drawn from their curve of rotatory dispersion. Furthermore, they failed to detect the anomalous dispersion in the blue of potassium iridioxalate,  $^{8,9}$   $K_3[Ir(C_2O_4)_3]$ . The pioneer researches of Jaeger cannot. therefore, be credited with more than a very moderate degree of accuracy.

It is probably correct to say that individual measurements of rotation within regions of strong absorption can seldom be relied upon more closely than to 5 per cent. of the absolute values, and often not as closely as this. The new polarimeter seems to yield results having about the same degree of trustworthiness. It is noteworthy that in the case of potassium cobaltioxalate, which is at present the only coloured compound to have been thoroughly examined by the new instrument, the molecular absorption coefficients are much larger than those of the majority of compounds investigated by Werner Kuhn.

The procedure adopted in studying the rotatory dispersion of coloured substances is as follows. A set is first made with a tube of sugar solution in holder A (Fig. 2) and a solution of the coloured racemate in B. Generally speaking, about five readings are taken of which the mean is given in the first column  $(\lambda_1)$  of the table below. Except in the far red, it is unusual for the extreme values to differ by more than three or four Angstrom units. It should be mentioned that if the tube of racemic solution is removed and another set made upon the centre of the black band, the reading is nearly always identical with the first, even in the neighbourhood of maximum absorption. Differences of one or two Angstrom units have sometimes been observed, but not systematically. and these can reasonably be attributed to the difficulty of locating the mid-point of the dark band which appears much broadened on account of the general reduction in the illumination of the field produced by the coloured solution. In practice, the zero readings  $(\lambda_1)$  have always been taken in the presence of racemic solution.

The next step is to insert in place of the racemate an equivalent tube of the optically active solution and again determine the position of the dark band. The mean readings appear in the second column  $(\lambda_2)$  of the table. From the values  $\lambda_1$  and  $\lambda_2$  and the Calibration Curve of the instrument, it is possible to calculate the optical rotation of the coloured solution at the wave-length  $\lambda_2$ , as previously described. A few typical results obtained with potassium d-cobaltioxalate are given in the following table:---

Å.	λ <u>1</u> Å.	l <sub>1</sub> cms.	l <sub>2</sub> cms.	$= \frac{\Delta l}{l_2 - l_1}.$	λ <sub>2</sub> Corrected.	$\sigma_{\lambda_2}$ .	R.	$R_0$ .
4929	4902	13.935	13·77	- ·165	4899	2·57°	- :43°	- ·48°
5582	5531	18.265	17·905	- ·36	5528	1·98°	- :71°	- ·77°
5794	5730	19.825	19·34	- ·485	5728	1·84°	- :89°	- ·95°
6340	6385	24.125	24·50	+ ·375	6400	1·45°	+ :54°	+ ·56°
6507	6569	25.525	26·04	+ ·515	6582	1·37°	+ :70°	+ ·73°

8 Ibid., 203, 1919.

<sup>9</sup> Bruhat. Bull. Soc. Chim., 17, 223, 1915.

<sup>&</sup>lt;sup>7</sup> Proc. Kon. Akad. Wet. Amsterdam, 21, 693, 1919.

The lengths of standard sugar solution,  $l_1$  and  $l_2$  (corresponding respectively to  $\lambda_1$  and  $\lambda_2$ ), are obtained from the Calibration Curve, and  $\Delta l$  is the difference between them. A correction is applied to  $\lambda_2$  on account of errors of graduation upon the wave-length drum of the spectrometer.  $\sigma_{\lambda_2}$  is the rotation per centimeter of the standard sugar solution at the corrected wave-length  $\lambda_2$ , derived by means of the dispersion equation of Lowry and Richards.<sup>3</sup> The measured rotation  $R = \Delta l \times \sigma_{\lambda_2}$  is recalculated to zero time from the known rate of racemisation at room temperature. The tabulated values of  $R_0$  differ appreciably from R, but these are the results of an early series of experiments. In recent work the correction has been rendered unnecessary by limiting the time of observation of the optically active solutions. The only toilsome step in the calculation of  $R_0$  from the observed wavelengths  $\lambda_1$  and  $\lambda_2$  is the evaluation of  $\sigma_{\lambda_2}$ , and this can be avoided by plotting Lowry and Richard's equation of rotatory dispersion on a large scale graph, and thereafter reading off the values of  $\sigma_{\lambda_0}$  directly. Thus the figures in columns 3, 4, 6, and 7 of the table can be rapidly ascertained from the corresponding graphs, and the labour of computation is reduced to an inconsiderable minimum.

## Summary.

A simple apparatus is described for the measurement of the variation of optical rotatory power with wave-length in the visible spectrum. It is designed, primarily, for the examination of coloured optically active compounds which undergo racemisation in aqueous solution. The method is probably capable of extension to the near ultra-violet. The outstanding advantages which the instrument possesses over the standard types of polarimeters are cheapness and ease of construction. Divided circles are dispensed with, and it should be possible in well-equipped physico-chemical laboratories to make the whole contrivance from spare parts and standard pieces of apparatus. The only unavoidable item of expenditure is a set of eight or ten polarimeter tubes. The new polarimeter is essentially suited to measurements of small rotations (one or two degrees, or less) and although making use of white light, the application is effectively monochromatic. The determination of rotatory power can be made at any number of wave-lengths. A disadvantage from which the instrument suffers is that the rotations are not read directly, but must be computed. The calculation is based upon the data given by Lowry and Richards for the rotatory dispersion of an aqueous solution of cane sugar.

The present apparatus has been shown to reproduce the rotatory dispersion of colourless compounds in a satisfactory manner. Under no circumstances, however, can the new model approach the accuracy of ordinary polarimeters in examination of transparent substances at specific wave-lengths, but it seems to be unique in preserving its very fair measure of reliability in regions of strong absorption.

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# STUDIES IN OPTICAL ACTIVITY, PART III. DEXTRO AND LAEVO COBALTIOXALATES.

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A severe obstacle to the quantitative study of optical activity is the fact that no really simple molecule can be expected to exist in optically isomeric forms. The most elementary type of organic compound necessarily consists of four dissimilar atoms or radicles united to an atom of carbon. Furthermore, the rotatory power of a substance at any specific wave-length represents the sum of the separate contributions of its active absorption bands, the influence of the nearest band being predominant as a general rule. Measurements of optical rotation at a few selected wave-lengths are therefore not fundamental numerical quantities, and on account of their composite nature are frequently very sensitive to changes of environment. The amazing similarity between the curves of rotatory dispersion of a host of colourless organic compounds in the visible spectrum is due to the fact that in all cases the nearest absorption band is. so to speak, infinitely far away in the ultra-violet. The real centre of interest from a theoretical standpoint is the disposition of the curve of rotatory dispersion in the immediate neighbourhood of the absorption bands. In this direction the recent researches of Werner Kuhn and his collaborators have proved extremely fruitful, but at the same time have revealed the limitations to which such investigations are subject. In no case was it possible to explore more than one electronic band, and this usually appeared merely as a hump upon the curve of general absorption which ascended so steeply as the wave-length diminished that further penetration was impossible.

Complex ions of the type  $[M(R_3)]^{---}$ , consisting of a central atom (or ion) of a transitional element and three oxalate ions each attached at two points to the metal, as though to the six corners of a regular octahedron, sometimes exhibit optical isomerism.1 The chromioxalate ion,  $[Cr(C_2O_4)_3]^{---}$ , is a well-known example. Relatively speaking, these ions are simple in constitution, and they usually possess two distinct absorption bands in the visible and near ultra-violet spectrum. In these respects they offer attractive opportunities for study, but some of them are photosensitive, and racemisation of the

optical isomers generally occurs in aqueous solution.

Our choice of potassium cobaltioxalate for the initial investigation was determined chiefly by the comparatively slow rate of racemisation of the salt in water. The substance has previously been examined by Jaeger and Thomas,2 but a number of important points were overlooked by these authors, and only a very moderate degree of accuracy was claimed for the measurements of rotatory dispersion. Their method of resolution was ill-adapted to the delicate nature of the compound. Thus,

<sup>&</sup>lt;sup>1</sup> Werner, Ber., 45, 3061, 1912; Johnson, Trans. Far. Soc., 28, 845, 1932.

equivalent quantities of aqueous solutions of strychnine sulphate and potassium cobaltioxalate were mixed; the precipitated strychnine salt was dissolved by addition of sufficient cold water, and the solution left to evaporate in an open vessel in the dark for several weeks at a temperature of about 16° C. Successive fractions of the strychnine salt were removed at intervals and converted to the potassium salt by treatment with potassium iodide (strychnine iodide is very insoluble) and precipitation of the potassium cobaltioxalate with alcohol. Only the

d-component was obtained in this way. This method was soon abandoned, for, owing to the slight solubility of the strychnine salt and the slow rate at which it goes into solution, quite unmanageable volumes of water were required. Moreover, the crops obtained on evaporation were small, and often contaminated with products of decomposition. The obvious plan of hastening evaporation by placing the solutions in evacuated desiccators containing sticks of caustic soda proved rather clumsy, and the crystals obtained varied very much in respect of optical activity. But one interesting fact was established, namely that the majority of the fractions possessed much larger rotatory powers than those recorded by Jaeger and Thomas. The marked increase was surprising, because evidence was presented in their paper purporting to show that the compound had been completely resolved. Their argument was as follows. Potassium cobaltioxalate was found to crystallise from water at temperatures above 13.2° C. as mixture of the two optically isomeric forms, and single crystals selected at random gave sometimes a lævo- and sometimes a dextro-rotation. The first crystal examined gave a curve of rotatory dispersion almost identical in magnitude though in opposite sense to that of the salt obtained from the crops of strychnine cobaltioxalate. This concordance was advanced as proof of the efficiency of the latter method of resolution, but our results show that it must have been fortuitous, and indeed that both samples of their active potassium salt contained nearly 90 per cent. of the racemic substance. Clearly Jaeger and Thomas's claim of spontaneous fission by crystallisation of potassium cobaltioxalate needs further investigation. Molecular rotations have been calculated by means of their formula, but whereas these authors credit potassium chromioxalate with larger rotatory power than potassium cobaltioxalate, our results show that the situation is reversed, even though the figures for the chromic compound have also been augmented.

No attention whatever seems to have been paid to the strychnine salt of cobaltioxalate, although it is obviously essential to concentrate upon it in order to find the best conditions for resolving the complex ion. This phase of the work has occupied us for a long time, progress being retarded by the difficulty of obtaining reproducible results and some very perplexing inconsistencies in behaviour. Reference is made in a subsequent paragraph to the discovery of an interesting property possessed by both the *d*- and *l*-strychnine salts which provides an explanation for many of the observed anomalies.\*

<sup>3</sup> Jaeger, Rec. Trav. Chim., 38, 202, 1919.

<sup>\*</sup>Throughout this paper constant reference is made to d- and l-cobaltioxalate. Since the rotation of the optically active salts changes direction at 6280 Å these terms are obviously arbitrary. In accordance with custom, we define the d and l salts as those possessing right and left-handed rotation, respectively, on the long wavelength side of the position of zero rotation.

## Experimental.

Potassium cobaltioxalate was prepared by the method of Sörensen <sup>4</sup> from analytically pure reagents. Gradual addition of absolute alcohol in the final precipitation of the salt from water ensures a beautifully crystalline product. The dark green crystals and their aqueous solution are decomposed by blue light and are somewhat unstable thermally, so care has been taken to avoid these circumstances.

Analysis. — The analytical results establish the constitution  $K_3[\text{Co}(\text{C}_2\text{O}_4)_3]$  .  $3\frac{1}{2}H_2\text{O}$  given by Jaeger and Thomas rather than  $K_3[\text{Co}(\text{C}_2\text{O}_4)_3]$  .  $3H_2\text{O}$  inferred by Sörensen. (Calculated  $(3\frac{1}{2}H_2\text{O})$ : oxalate 52·5 per cent., cobalt II·5 per cent., water I2·5 per cent. Found: oxalate 52·2  $\pm$  0·I per cent., cobalt II·6  $\pm$  0·I per cent., water I2·I  $\pm$  0·2 per cent.).

## Method of Resolution.

One gm. of potassium cobaltioxalate is dissolved in 10 to 20 c.c. of water and then about IIO c.c. of a saturated solution of neutral strychnine sulphate is added in approximately equivalent amount. The precipitated strychnine cobaltioxalate is filtered off and dried first by suction and subsequently upon a porous tile. This is strongly lavorotatory at the wave-lengths 5893, 5780, and 5461 Å., and the filtrate dextrorotatory. A number of lævorotatory residues can be prepared in this way and mixed together. The whole is then quickly extracted with successive quantities of warm water (30° to 40° C.), and the aqueous extracts placed in a bath of crushed ice. In an hour or so considerable quantities of glistening flaky crystals have deposited in all the beakers, and when separated and dried are found to be even more strongly lavorotatory than the original mixture. Repetition of the extraction and freezing process twice or thrice produces crystals having a lævo-rotation which is not increased by further treatment, and of which the rotatory power is approximately 50 per cent. higher than that of the original residue. Obviously, this procedure is extremely wasteful, and the ultimate yield of highly active salt is small; but, fortunately, small amounts suffice for measurements of rotatory dispersion and absorption. In point of fact, the complete curve of rotatory dispersion can be obtained with 0.2 gm. of the strychnine salt, but to secure a satisfactory yield of optically active potassium cobaltioxalate 3 or 4 gms. must be prepared.

The dextrorotatory filtrate is placed in the ice bath and being saturated, presumably, with respect to the strychnine salts of d- and l-cobaltioxalate it should deposit a mixture of these compounds in proportions depending on the relative trend of the solubility curves between room temperature and 0° C. Some irregularities might be anticipated on account of the extraordinary degree to which aqueous solutions of strychnine salts may remain supersaturated, and because of conceivable peculiarities in the rates of crystallisation. But our observations have confounded all expectations. The precipitates obtained in the initial experiments were optically inactive at 5461 Å., and therefore seemed to be mixtures of the two compounds in which a slight preponderance of the l salt neutralised the small rotation of strychnine ion. The lævorotation of the latter at the concentrations used in polarimetric measurements amounted to barely  $0.05^{\circ}$ , whereas lævorotatory strychnine cobalti-

oxalate gave readings of about 0.8°. Recently, in trying to repeat the experiments, we obtained not pseudo-racemic mixtures but strongly dextrorotatory crystals which were shown by calculation to be almost as pure as the best lævorotatory samples. Unfortunately, the result cannot be reproduced at will; only three attempts out of twenty have been successful. In the hope of eliminating this irregularity, we have investigated the effect of changing the concentrations of the reactants, the temperature of initial precipitation, hydrogen-ion concentration, and have employed more than one preparation of potassium cobaltioxalate and strychnine sulphate, but to no purpose. Inconsistencies of this sort have also been encountered during experiments on the crystallisation of the strychnine salts from water.

The important experimental fact is that strychnine *l*-cobaltioxalate has been isolated. This was not accomplished by Jaeger and Thomas. Attempts made to enhance the rotation along the lines indicated in the case of the other optical isomer were unsuccessful, and resulted in the diminution of the rotatory power.

The best means of preparing optically active potassium salts from the strychnine compounds is that recommended by Werner, in which strychnine salt is treated with potassium iodide solution, the insoluble strychnine iodide removed by filtration, and the potassium salt precipated with alcohol. In order to minimise racemisation, the solid strychnine salts were added to an excess of ice cold aqueous potassium iodide, triturated for five minutes, filtered, and precipitated with ice cold absolute alcohol. One reprecipitation was performed in a similar manner. The whole operation occupied about ten minutes, so the amount of racemisation cannot have been appreciable. Incidentally, the rate of racemisation was shown to be unaffected by the presence of potassium and iodide ions. But the method is not entirely satisfactory, and the yield of potassium salt is poor. Other means of converting strychnine compounds to the potassium salts were tried, but none proved successful.

A convenient method for preparing potassium *l*-cobaltioxalate is the following. Solutions of the racemic salt and of strychnine *nitrate* are mixed in equivalent proportions and the precipitate of strychnine cobaltioxalate removed by filtration. A small excess of solid potassium iodide is added to the filtrate, which precipitates all the strychnine as strychnine iodide. After filtration, just sufficient absolute alcohol is added to the clear solution to throw out the potassium salt. On account of the uncertainties attending the preparation of strychnine *l*-cobaltioxalate this method is of considerable value, for highly active specimens of potassium cobaltioxalate can be obtained, although there must necessarily be present some racemic compound. Strychnine nitrate is used instead of strychnine sulphate in the first step because potassium nitrate is considerably more soluble in aqueous alcohol than potassium sulphate, and thus contamination of the optically active salt is avoided.

### Analytical.

The strychnine salts were analysed for strychnine, oxalate, and water of crystallisation, and shown to be tri-strychnine derivatives possessing the general formula  $(Str)_3[Co(C_2O_4)_3] \cdot xH_2O$ . The only possible contaminants were potassium, sulphate, and hydrogen ions, and these were ruled out by qualitative tests.

Strychnine.—Unsuccessful attempts were made to estimate the strychnine gravimetrically, (a) as strychnine iodide, (b) as strychnine picrate. 5 and (c) as strychnine, by extracting the base with chloroform in the presence of concentrated ammonium hydroxide.6 The first method failed on account of the pronounced tendency of the solutions to remain supersaturated, the second because of adsorption of picric acid by strychnine picrate, and the third owing to interaction between cobaltioxalate and chloroform which caused contamination of the strychnine. The results from (c) were about 3 per cent. too high, but at any rate proved that the compounds were tri-strychnine salts. Eventually the total nitrogen was estimated by means of a suitably modified Dumas combustion. Approximately 10 c.c. of nitrogen were collected in each analysis, so the method cannot be described as micro-analytical, but the micro-analytical technique formed the basis of our procedure. We are indebted to Dr. M. Nierenstein for providing a gas burette which could be read accurately to 0.05 c.c. and for much helpful advice. Excellent analytical results were obtained which confirmed our opinion that the high values hitherto recorded were spurious.

Water.—The water of crystallisation has been estimated in two ways; by dehydration over phosphorus pentoxide in highly evacuated desiccators in the dark, and by determining the loss of weight at 110° C. The second method is merely a check upon the first, since thermal decomposition involves a loss of carbon dioxide also, but the percentage loss of carbon dioxide varies so little with different degrees of hydration of the strychnine salt that the water content can be inferred to a close approximation. This method gives smaller and more variable figures than the other, which indicates that the expulsion of carbon dioxide from the solid is incomplete, a fact which may be connected with the mechanism of thermal decomposition within the crystal. Thus,

(1) 
$$[Co(C_2O_4)_3]^{--} \rightarrow [Co(C_2O_4)_2]^{--} + C_2O_4^{--}$$
  
(green) (pink)  
(2)  $2C_2O_4^{--} \rightarrow C_2O_4^{--} + 2CO_2$ .

In the first step, an electron which has been shared between the cobalt and the oxalate instantaneously becomes the exclusive property of the former, the transfer being accompanied by a change of colour from green to pink. The second step is conceivably slow.\* Crystals of strychnine cobaltioxalate decompose rapidly at temperatures above 80° C., but the potassium salt is more stable and even at 110° C. only slowly turns pink. In this case also, the hydration figure is lower than that obtained by desiccation over phosphorus pentoxide. The latter process occupies about ten days, and the fact that constant weight is eventually reached precludes the possibility that the disagreement between the results of the two methods is due to some decomposition accompanying dehydration.

Oxalate.—It is first essential to remove the strychnine, and this is best done with ammonium hydroxide and chloroform, as previously mentioned. Precipitation of calcium oxalate proved unsatisfactory, so

<sup>&</sup>lt;sup>5</sup> A. W. Blyth, Poisons: Their Effects and Detection, 1890.

<sup>&</sup>lt;sup>6</sup> British Pharmacopæia, p. 119, 1914.
\* The photochemical decomposition seems to follow the same course. If a single orthorhombic crystal of strychnine cobaltioxalate is exposed to blue light, subsequent microscopic examination fails to reveal any change other than that of colour, but after the lapse of a day or two cracks appear on the surface, presumably caused by the escape of carbon dioxide.

the gravimetric method was abandoned in favour of direct titration against potassium permanganate. After extraction of the strychnine, the ammoniacal solution was boiled with excess of sulphuric acid in order to expel dissolved chloroform and decompose the complex ion, and titrated against 0.02 N permanganate. The thermal decomposition of cobaltioxalate in hot acid solution is accompanied by the oxidation of one-sixth of the oxalate, and in this connection an important observation has been made. If the ammoniacal solution (above) is decomposed by boiling prior to the addition of acid, appreciably more permanganate is used in the titration than if the solution is acidified before heating. explanation is that cobaltic ion is partly precipitated as cobaltic hydroxide in hot alkaline solution, and therefore a portion of the oxalate escapes oxidation. The method of analysis of  $K_3[Co(C_2O_4)_3]$  recommended by Sörensen 4 involves the precipitation of the cobalt with potassium hydroxide, and this, doubtless, is the cause of his high results. Further difficulties have been encountered in the analysis and consequently the figures given below are only approximate.

#### Results.

Strychnine d-cobaltioxalate (13 $\frac{1}{2}$ H<sub>2</sub>O), Calculated: nitrogen 5·35 per cent., water 15·5 per cent., oxalate 16·8 per cent. Found: nitrogen 5·38  $\pm$  ·04 per cent., water 15·4  $\pm$  0·3 per cent., oxalate 17·0  $\pm$  0·5 per cent.

Strychnine *l*-cobaltioxalate (9½ $H_2O$ ), calculated: nitrogen 5.60 per cent., water II·4 per cent., oxalate I7·6 per cent. Found: nitrogen 5.58  $\pm$  0.05 per cent., water II·4  $\pm$  0·4 per cent., oxalate I7·7  $\pm$  0·5 per cent.

The analyses indicate that a molecule of the d-salt is associated with 13 or 14 molecules of water in the crystal, and the l compound with 9 or 10. Both are dull green in colour, are neither efflorescent nordeliquescent, and appear to crystallise in the orthorhombic system.

Only small quantities of optically active potassium salts have been obtained, because the yield of pure material from active strychnine salts is poor. The analytical figures for oxalate and water are fairly consistent and suggest the approximate formula  $K_3[\text{Co}(\text{C}_2\text{O}_4)_3]$ .  $2\text{H}_2\text{O}$  for both the d- and l-compound. The preparations were dried by treatment with alcohol and ether, which may account for the fluctuations (1.8 to 2.5 molecules of water per mol. of salt) actually observed.

### Rotatory Dispersion.

Measurements of the variation of rotatory power with wave-length have been made by means of the polarimeter described in Part II, which appears concurrently with this paper. Equi-molecular solutions were prepared by dissolving 0.0156 gms. of the optically active potassium cobaltioxalates, and 0.0520 and 0.0494 gms. of the d- and l-strychnine salts, respectively, in 100 c.c. of aqueous solution. These were examined throughout the spectrum in a 30 cm. polarimeter tube. Determinations at two wave-lengths, 5461 Å and 5780 Å were also made in a Schmidt and Haensch polarimeter (crosses in Fig. 1), but to accomplish this, the length of tube had to be reduced to 20 cms. The strength of the solutions is only  $3 \times 10^{-4}$  molal, yet ten or fifteen minutes of vigorous shaking is required to dissolve the strychnine d-salt, which shows a remarkable reluctance to pass into solution. The curves of rotatory dispersion of

the potassium and strychnine salts of d- and l-cobaltioxalate are shown graphically in Figs. 1 and 2. In Fig. 1 the measured values of rotation in the neighbourhood of the absorption band are plotted against wavelength in order to illustrate the degree of reproducibility of individual readings. In Fig. 2 the complete curves are drawn on a smaller scale, together with the corresponding absorption coefficients. The contribution of strychnine ion to the observed rotations of the strychnine salts is also indicated. The absorption of the coloured solutions was determined by means of a Hilger-Nutting spectrophotometer and the molecular absorption coefficients calculated from the relationship  $I/I_0 = 10^{-\alpha tc}$ ,  $\alpha$  being the molecular absorption coefficient, t the thickness in cms. of the coloured solution, and c the concentration in mols. per litre.

 $K_3[Co(C_2O_4)_3]$ .—When comparing the curves of rotatory dispersion of the optically active potassium salts, it is important to realise that the

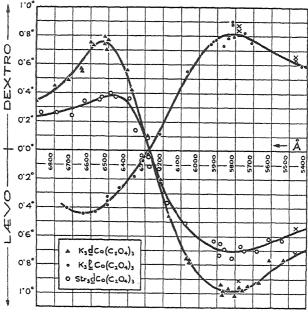
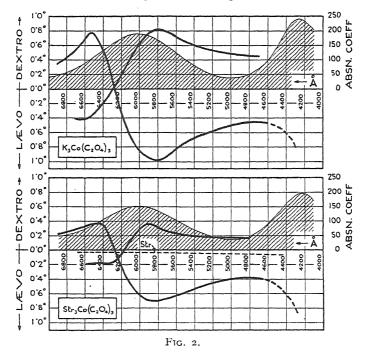


Fig. 1.—Observed Rotations.

d-salt was the purest yet obtained, whereas the l compound certainly contained a proportion of racemate, which accounts for its somewhat smaller rotatory power. The striking fact about the curves is that they are not exactly complementary. The axis of zero rotation is crossed at about the same wave-length, 6280 Å, but the relative magnitudes of the two maxima of rotation are not identical. Thus, for the  $\bar{l}$ -cobaltioxalate the ratio of maximum rotation in the yellow to that in the red is approximately 1:0.5, whereas in the case of the d-salt it is 1:0.75. Another peculiar feature is that the general contour of the dispersion curves in the red is not the same. The d-salt gives a fairly sharp maximum of rotation around 6550 Å, whereas the l-salt has a much smoother curve with a maximum at about 6650 Å. In the latter case the rotation at 6700 Å is still almost equal to that at the maximum, but for the d-salt it is 30 per cent. lower than the maximum value. These results are contrary to

the accepted principle that d and l forms of a compound are identical in rotatory power though opposite in sign.

The discrepancy could be caused by contamination of the active cobaltioxalates with an optically active impurity, or by errors inherent in the polarimetric method. The presence of an optically active impurity is extremely improbable. Strychnine is ruled out, since its contribution to the rotation of the tri-strychnine compounds is almost inappreciable (Fig. 2). An active form of cobaltioxalate can be imagined in which two cobalt atoms are linked by oxalate radicles, but there is no positive evidence of its existence. The absorption spectra of the cobaltioxalates are closely similar, and the d-and l-potassium salts racemise completely, and at the same rate, in aqueous solution. Polarimetric defects, if present, must be such as to produce too high dextrorotations and low



lævorotations, but this is contrary to observation, as may be seen from Fig. I by comparing the points obtained with the new polarimeter and those recorded on the Schmidt and Haensch instrument. Now the sensitivity of the eye diminishes in passing from yellow to red, and it may be suspected that displacements of the dark band (Part II. gives instrumental details) towards the long wave-lengths by a dextrorotatory substance, are accompanied by unsymmetrical broadening of the band in the same direction, and hence give rise to spuriously large values of dextrorotation in the red. The supposition has been tested and shown to be false; moreover, had this been the cause of the apparent anomaly, it must have affected the relative contours of the long wave-length maxima in a manner opposite to that actually observed.

Nevertheless, it is a fact that racemic potassium cobaltioxalate is completely devoid of rotatory power at all wave-lengths, and this cannot be reconciled with the differences in the curves of rotatory dispersion of the two optically active components unless some kind of interaction (readjustment) takes place, when they are brought together in aqueous solution. A solution containing 0.0084 gm. of the l-salt, and 0.0072 gm. of the d-salt in 100 c.c. of water was found to be practically racemic (there was an apparent slight excess of the l-salt), whereas calculation based upon the dispersion curves predicted zero rotation in the yellow and marked dextrorotation in the red.

The curves of rotatory dispersion have been re-examined at points in the neighbourhood of the maxima, making use of new preparations of potassium *d*- and *l*-cobaltioxalate. The discrepancies remain. Much further work is contemplated, but progress is necessarily slow.

No significant differences have been detected in the absorption of aqueous solutions of the racemate and the optically active isomers, either as regards the location of maximum absorption or in the absolute values of the molecular absorption coefficients.

(Strychnine)<sub>3</sub> [ $Co(C_2O_4)_3$ ].—It can be seen from Fig. 2 that the molecular rotatory power of the strychnine salt of *d*-cobaltioxalate is considerably less at all wave-lengths than that of the potassium salt which was prepared from it, and that the strychnine salt of the *l* compound is still less active.

It has recently been discovered that the solid strychnine salt of d-cobaltioxalate loses about one-quarter of its rotatory power in a week or so after preparation, and then remains without further change for an indefinite period. On the other hand, crystals of the strychnine salt of l-cobaltioxalate completely lose their dextrorotation at 5461 Å in the course of a couple of months at room temperatures, becoming slightly lævorotatory on account of the strychnine content. Conversion to the potassium salt results in the separation of racemic potassium cobaltioxalate.\* In order to understand the differences between the curves in Fig. 2 it is necessary to consider these facts in relation to the history of the compounds. The strychnine salt of d-cobaltioxalate was prepared, and three days later a portion of it was converted to the potassium salt, and this and the remainder of the strychnine salt were used to determine the curves of rotatory dispersion. Measurements were commenced rather more than a week after the preparation of the strychnine compound. The potassium salt of l-cobaltioxalate was obtained from the corresponding strychnine derivative about a week after the preparation of the latter, but measurements of rotatory dispersion were not begun until a month from that date. Therefore the curve of rotatory dispersion of strychnine d-cobaltioxalate is that of the compound in its steady state, but the racemisation of the corresponding l-salt was already far advanced when the measurements were made. The apparent displacement of the position of zero rotation is partly due to the superposition of the lævorotation of strychnine, which is relatively large in this case, but

<sup>\*</sup> These observations are at present being extended in a number of directions and, apart from their intrinsic interest, promise to throw light on many of the perplexing inconsistencies encountered during the research. As far as we know, this is the first example of racemisation of a complex ion occurring in the crystalline state. The difference in behaviour of the strychnine salts of d- and l-cobaltioxalate in regard to racemisation may conceivably bear upon the anomalies already discussed in connection with the rotatory dispersion of the corresponding potassium salts in solution, although at ordinary temperatures neither potassium salt shows any sign of undergoing racemisation in the solid state.

for obvious reasons no great reliance can be placed upon this particular curve.

It is noteworthy that the maxima of absorption of strychnine d-co-baltioxalate in aqueous solution occur at the same wave-lengths as for the corresponding potassium salt, but the molecular absorption coefficients are distinctly less. The photometric measurements were made soon after the preparation of the compound, but whether this is true in the case of absolutely fresh material has not yet been ascertained. Probably it is, because the curves obtained for strychnine d- and l-cobaltioxalates were identical within the limits of accuracy of the instrument (about 3 per cent.).

### Discussion.

The molecular rotatory power of potassium d-cobaltioxalate is extraordinarily large; probably the largest yet recorded for a pure compound in the neighbourhood of an active absorption band.\* Our measurements are shown graphically in Fig. 3 (curve I) with those of Jaeger and Thomas (curve 3), and it is obvious that their compound was very far from being completely resolved. These authors state that their results are somewhat uncertain, so the differences in the character of the dispersion curves are not surprising. The molecular rotations were calculated according to the formula used by Kuhn and Braun, that is, the product of the rotation per decimeter length and the molecular weight, divided by the percentage composition of the solution. The figures supplied by Jaeger and Thomas in their paper have been divided by ten in order to make them comparable.

An interesting feature of the curve of rotatory dispersion of  $[Co(C_2O_4)_3]^{---}$  is the displacement of the position of zero rotation some 250 Å to the long wave-length side of the maximum of the absorption band. Werner Kuhn and Szabo 8 observed a displacement almost identical in amount but towards the short wave-lengths in the case of a complex aqueous solution of "potassium chromic tartrate," and from measurements of circular dichroism proved that the absorption band itself possessed a corresponding complexity, being compounded of more than one type of molecular vibration. We have recently found that the dispersion curve of potassium chromioxalate shows a shift of the position of zero rotation of about the same magnitude and in the same direction as that of the complex tartrate. This is especially interesting, because we are dealing here with a molecular ion of definite constitution. Thus the phenomenon may eventually prove to be a general one, connected with the peculiar nature of the broad absorption bands. An alternative explanation in the case of cobaltioxalate is to assume that an active absorption band in the ultra-violet, of opposite sign to that at 6020 Å, is making an appreciable contribution to the optical rotation in the visible spectrum. This would have the effect of shifting the zero point towards the long wave-lengths. There is some support for this idea from the trend of the dispersion curve in the blue in Fig. 2, but this part of the curve is dotted because the points are not yet sufficiently well established. The strong absorption in the band at 4250 Å and the high dispersion of the spectrometer permit the use of only 10 cm. length

<sup>\*</sup>Our work on the corresponding salt of chromium is incomplete, but the figures appear to approach the same order of magnitude.

7 Z. physik. Chem., 8B, 281, 1930.

8 Ibid., 15B, 59, 1931.

of optically active cobaltioxalate solution, and consequently the readings are liable to large errors. On the supposition that the dotted curve is correct, it appears hardly likely that this absorption band is active, so the activity must arise from one lying in the ultra-violet. In order to test this point, we propose to explore the relatively transparent region between 3800 Å and 3300 Å.

The conspicuous symmetry of the sinuous curve of rotatory dispersion with respect to the zero axis of rotation justifies an attempt to analyse it by the method of Kuhn and Braun. In the absence of measurements of circular dichroism, the analysis can only be performed in an approximate manner by selecting likely values of the important constants. However, this arbitrary procedure was used very success-

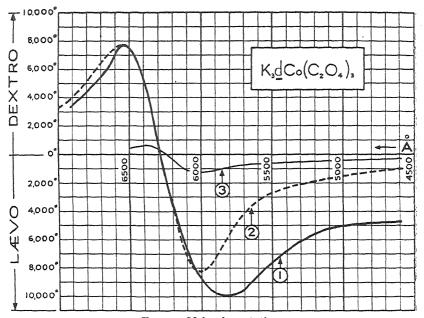


Fig. 3.—Molecular rotations.

fully by Kuhn in his early work. The following constants were chosen (or derived):

$$[\Phi] = 134.4$$
,  $\theta = 0.22 \times 10^{14}$ ,  $\nu_0 = 4.78 \times 10^{14}$ ,  $\nu_{\phi} = 4.58 \times 10^{14}$ .

Their significance will be explained in a subsequent paragraph. The computed curve of molecular rotatory power is shown graphically in Fig. 3 (curve 2). Comparison of curves I and 2 reveals satisfactory concordance in the red, and very poor agreement in the region of shorter wave-lengths. But if the assumption is made that the experimental curve, I, contains a significant contribution of lævorotation at all wave-lengths from an active band in the ultra-violet, the modified experimental and calculated curves can be brought into close correspondence, for the effect is to increase the values of  $[\Phi]$ ,  $\theta$ , and  $\nu_0$  and consequently eliminate the present discrepancy at the maximum of rotation in the yellow. This assumption has already been advanced, tentatively, on other grounds, but it is impossible to draw a definite conclusion until measurements of circular dichroism have been made.

According to Kuhn's theory of optical activity, coupled vibrators are responsible for the optical rotatory power of a molecule, and one of the most interesting results is that the distance separating the resonators can be calculated from relevant data. The following equations were derived.

$$g_0 = \frac{2\sqrt{\pi}\nu_0[\Phi]}{2\cdot303\times\cdot541\times100\times\alpha_{\max}\times\nu_{\phi}} \simeq \frac{2\cdot85\ [\Phi]}{100\ \alpha_{\max}}, \quad . \quad (1)$$

 $g_0$  is the anisotropy factor (or coupling factor) which primarily controls the optical rotatory power, that is, the rotatory dispersion and circular dichroism, of an active absorption band.  $\nu_0$  and  $\lambda_0$  are the frequency and wave-length, respectively, of zero rotation on the dispersion curve.  $\nu_{\phi}$  is the frequency corresponding to the maximum of rotation on the long wave-length side of the absorption band, and  $[\Phi]$  radians is the molecular rotation at this point.  $\alpha_{max}$  is the molecular absorption coefficient at the position of maximum absorption; d is the distance referred to above. Equation 2 is derived for the case of a vibrating electric moment possessing two components of the same magnitude, perpendicular to each other, and separated by the distance d. departure from either or both of these conditions has the effect of making the calculated distance smaller than is actually the case. Incomplete resolution of the optical isomers affects the result in the same way, and another factor operating adversely is that the measured absorption coefficient (which occurs in the denominator) is likely to consist of inactive as well as active vibrational components. The calculated value of d is therefore a minimum. Yet the striking fact which emerges from Kuhn's researches is that in all cases the calculated distances are surprisingly large in relation to the probable molecular dimensions. Thus, for the active absorption band of the azide radicle (N<sub>2</sub>) in the methyl ester of azidopropionic acid, and the dimethylamide of the same acid,  $d_{\min}$  is approximately equal to 3 and II Ångstrom units respectively.7 Kuhn has therefore concluded that the conditions stipulated in the derivation of equation 2 are complied with in all cases, a conclusion which seems highly improbable on general grounds. Further doubts as to the true significance of the calculated distances arise from Kuhn and Szabo's data 8 on aqueous solutions of "potassium chromic tartrate." For this substance,  $d \ge 80 \text{ Å}!$  This extraordinary result is attributed to the formation of large "loose" compounds between the chromic and tartrate ions, their interaction being conceived as a kind of resonance rather than the formation of chemical bonds. But, according to an hypothesis recently developed by one of  $us,^1$  an interaction of this sort is incapable of producing anisotropy in the absorption bands of chromic ion. Moreover, the chromic ion is particularly well suited to the formation of electron pair bonds 9 and a number of possible structures for chromitartrates can be imagined, some of which involve more than one chromic ion linked together by tartrate radicles. The rotatory power of such a complex solution might be expected to be sensitive to dilution which was what Kuhn and Szabo observed. But  $d_{\min} \ge 80 \text{ Å}$  is extremely difficult to accommodate on any theory.

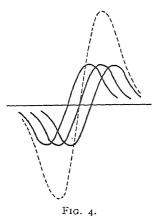
In the light of these considerations, it is interesting to find that for

<sup>&</sup>lt;sup>9</sup> Linus Pauling, J.A.C.S., 53, 1367, 1931.

cobaltioxalate,  $[\text{Co}(\text{C}_2\text{O}_4)_3]^{--}$ ,  $g_0 = 2 \times \text{IO}^{-2}$ , and  $d_{\min} = 20 \text{ Å}$ , which is much larger than can be accounted for from the likely dimensions of the molecular ion. The polarimetric measurements were made on 0.0003 molal solutions of the potassium salt, at which concentration the average distance separating the optically active ions was fully 150 Å. The rotatory power was unaffected by dilution.

It is obvious from equations 1 and 2 that the large calculated values of  $d_{\min}$  must be related to large values of the anisotropy factor,  $g_0$ , and therefore the measured quantity  $g_0$  may actually represent a summation of these terms. It is desirable to find a physical basis for this conclusion. Werner Kuhn's model of the optically active molecule consists essentially of coupled resonators which are responsible for the absorption as well as the rotatory power. The resonators are sometimes described as vibrating electric moments and sometimes as vibrating electrons, although these terms are no longer used by spectroscopists. In what follows, an attempt is made to present the theory from the standpoint of molecular spectra.

One of the most striking contributions ever made to the study of



optical activity is the beautiful work of Kuhn and Lehmann <sup>10</sup> on  $\beta$ -octyl nitrite. This compound possesses an absorption band in the near ultra-violet resolvable into five vibrational heads, each of which is shown to produce an anomalous (i.e. sinuous) curve of rotatory dispersion. It is therefore reasonable to postulate that an absorption band must possess vibrational components if it is to give rise to optical activity, the anisotropy being acquired by coupling of its vibrational levels with those of other vibrators in distant parts of the molecule. Each vibrational component of an active band will make a specific contribution to the optical activity.\* So far,  $\beta$ -octyl nitrite is the only case in which an

active absorption band has given spectroscopic evidence of structure. The broad active absorption band of potassium cobaltioxalate (Fig. 2) is a particularly clear example of the symmetrical but unresolvable type. Doubtless these bands consist of overlapping vibrational components. In Fig. 4 is illustrated the effect of summation of a number of closely spaced curves of anomalous rotatory dispersion. The summation curve (dotted) is seen to be quite smooth and apparently regular, just as observed in the case of cobaltioxalate. But the absorption coefficients of the corresponding band heads must also appear as a sum of these quantities in the measured curve of absorption, and since the anistropy factor is a ratio of rotatory power to absorption (equation I), the two effects may neutralise one another, and therefore the existence

10 Z. physik. Chem., 18B, 32, 1932.

<sup>\*</sup>As a corollary it follows that an absorption "band" which is the result of a pure electron transition cannot promote optical rotatory power. The optically active complex salts of chromium are characterised by narrow lines in the red. There is no evidence from the work of Jaeger or Kuhn and Szabo that they make any appreciable contribution to the rotatory power, but we are studying various optically active compounds in order to be quite sure.

of overlapping vibrational bands is not in itself capable of accounting for the incredibly large calculated values of  $d_{\min}$ . The explanation is perhaps the following. The theory 11 which led to the derivation of equations I and 2 is based upon the interaction of two characteristic frequencies of vibration, the essential condition being the coupling between them, although, apparently, weak coupling suffices to generate optical activity. Now weak coupling of the vibrational components of an electronic band with another characteristic frequency will cause scarcely appreciable changes in the energy levels involved in producing the absorption band, and hence affect the absorption to an insignificant degree. But the coupling concerns several vibrational levels, and may actually extend to a number of different vibrators in the molecule, and this will increase the anisotropy (and hence the rotatory power) much in the same way that an increase in the number of electrons in an atom or molecule enhances the ordinary refraction. For optical activity is but a very minute per turbation of ordinary refraction, being in fact a small circular double refraction as realised a hundred years ago by Fresnel, and thus there appears to be a distinct parallelism between the two effects. Here, then, is a phenomenon which can strongly influence the contribution of the vibrational components of an absorption band to optical activity

without increasing its absorption, which is just what is required to explain the large calculated values of  $d_{\min}$ . The conditions governing the coupling of resonators in a molecule are uncertain, but presumably the probability of interaction is greater the closer the approach of the energy levels, and the nearer the resonators are together. Optical activity is therefore likely to attain a high degree in dissymmetric molecules possessing a set of identical, or nearly identical, frequencies of vibration. Ions of the cobaltioxalate type are good examples,

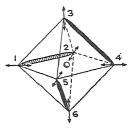


FIG. 5.

since the co-ordinated groups are all the same and the six electron pair bonds uniting them to the central atom are equivalent in strength and direction.9 As may be seen from Fig. 5, the octahedral symmetry of compounds having co-ordination number six is particularly favourable to the development of optical activity. In the case of cobaltioxalate, the three oxalate radicles are doubly attached to the cobalt at positions (1, 2), (3, 4), and (5, 6). Presumably the characteristic vibrations will be executed chiefly in the direction of the valence bonds which are at right angles to one another, and hence fulfil one of Kuhn's requirements 11 for optimum rotatory power, which are that the coupled vibrators be at right angles and separated by a finite distance in relation to the beam of polarised light. Considering, for example, vibrator 6, it is evident that under no circumstances can its interaction with vibrator 3 promote activity since the vibrations are parallel, and that the nett result of coupling with 1, 2, 4, and 5 will depend upon the path of the ray through the molecule. Thus, if the light is assumed to pass in a direction parallel to a line through 3 and 6, the vibrator 6 may interact effectively with these four oscillators, but if the molecule be rotated through 90° about the 2, 5 axis, vibrator 6 becomes coplanar with 2 and 5, in relation

<sup>&</sup>lt;sup>11</sup> Werner Kuhn, Z. physik. Chem., 4B, 14, 1929; Trans. Far. Soc., 26, 293, 1930.

to the beam of light, and their mutual influences cease to contribute to the optical activity. If an isotropic crystal could be obtained, the variation of rotatory power with direction might be studied from this standpoint, but unfortunately no suitable co-ordination compound appears to crystallise in the cubic system, and attempts made here to prepare alums from the sulphate of the tri-ethylene-diamine compound of chromic ion,  $Cr(en_3)^{+++}$ , have (as expected) proved futile.

## Summary.

A satisfactory method of resolution of  $[Co(C_2O_4)_3]$  - - into its optical isomers has been developed by taking advantage of the difference in solubility of the strychnine salts; and the isolation of strychnine l-cobaltioxalate has been accomplished for the first time. The analyses, absorption coefficients, and measurements of the variation of rotatory power with wave-length for the potassium and strychnine compounds of d- and lcobaltioxalate are presented in detail. The molecular rotatory power of potassiun d-cobaltioxalate is probably the highest yet recorded in the case of a pure substance.

The curves of rotatory dispersion are not symmetrical with respect to the active absorption band, the position of zero rotation (6280 Å) being displaced some 250 Å towards the long wave-lengths from the maximum absorption at 6020 Å. The anisotropy factor,  $g_0 \simeq 2 \times 10^{-2}$ , and  $d_{\min} \simeq 20$  Å, the latter (according to Werner Kuhn) representing the minimum distance separating the components of the vibrating electric moment responsible for optical activity. This surprisingly large value of  $d_{\min}$  and others obtained by Kuhn and his collaborators are discussed, and an hypothesis put forward to explain them.

The strychnine salts of d- and l-cobaltioxalate crystallise, respectively, with 14 and 10 molecules of water. The solid l-salt racemises completely if kept for a few weeks, whereas the d-salt quickly loses about 25 per cent. of its activity and then remains practically unchanged for as long as we have been able to observe it. This is the first example of a molecular ion

undergoing racemisation in the crystalline state.

One of us (A. M.) wishes to express his gratitude to the Department of Scientific and Industrial Research for a maintenance-grant.

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# A STUDY OF THE SYSTEM WATER-PHENOL. PART III. ELECTRICAL CONDUCTIVITIES.

By Owen Rhys Howell and Cecil Handford.

Received 6th March, 1933.

The densities 1 and viscosities 2 of solutions in this system have already been published.

For the determination of the electrical conductivities, special precautions have had to be taken to obtain both water and phenol in a high state of purity and to prevent contamination of the solutions by electrolytes.

<sup>&</sup>lt;sup>1</sup> Howell, Roy. Soc. Proc., 137, 418, 1932. <sup>2</sup> Howell, Trans. Farad. Soc., 28, 912, 1932.

Since it was deemed desirable in determining the conductivity at each concentration to use the same solution at each working temperature, six thermostats were used. These were gas-heated from a governed supply and maintained at 20°, 30°, 40°, 50°, 60° and 70° to within  $\pm$  0.01°.

A highly accurate and convenient method of measuring electrical conductivities has been developed and proved to be very satisfactory.

# Experimental.

## Preparation of Pure Water.

Water of very low conductivity can be prepared by simple distillation after addition of various reagents, 3 or by sweeping over gaseous impurities in a current of air freed from carbon-dioxide, 4 or by fractional condensation so that the impurities are carried on in the remaining steam.<sup>5</sup> A combination of the last two methods has also been used. 6 We have adopted the fractional condensation method which has the advantage of simplicity and has been found remarkably dependable in its yield and quality of distillate.

A copper boiler which holds about 30 litres is lagged with asbestos sheet and heated by a ring burner, the gas supply being carefully regulated and read on a manometer. The boiler is fitted with a long tube to act as a safety valve. The steam outlet tube and the whole of the remainder of the apparatus with which the steam and condensate come in contact is made of half-inch pure tin tubing. For the screw-joints the tin tube is expanded and accurately faced so that on tightening up the brass screws the two tin faces make a steam-tight joint. All other joints are welded with pure tin only. The spray-trap consists of twenty turns of the tubing leading into a circular box fitted with a baffle where the spray settles and is run off through a constant level trap. The whole trap is enclosed in a wooden box loosely packed with cotton-wool, and the tubes leading to the condensers are also lagged with cotton-wool. The first condenser is partly filled with transformer oil through which a regulated current of air is drawn to secure the requisite amount of condensation. The condensed water runs back through a trap (to prevent passage of steam in that direction) and is cooled before collection. The uncondensed steam passes through a second condenser and affords a supply of secondary water.

The still will deliver consistently per hour about 120 c.c. of primary water having a conductivity of about  $0.4 \times 10^{-6}$ , and about 300 c.c. of secondary water having a conductivity of about  $1.2 \times 10^{-6}$ .

## Phenol.

As in the previous investigations, the phenol was prepared by distilling the pure commercial product and accepting only the middle fraction. Distillation was performed in an apparatus made entirely of quartz and the phenol distilled into a quartz tube for the preparation of the water-rich solutions (up to 10 per cent. phenol) and directly into the

<sup>&</sup>lt;sup>3</sup> Walker and Cormack, J. Chem. Soc., 77, 5, 1900; Kendall, J. Amer. Chem.

Soc., 38, 2460, 1916.

<sup>4</sup> Bourdillon, J. Chem. Soc., 103, 791, 1913.

<sup>5</sup> Kraus and Dexter, J. Amer. Chem. Soc., 44, 2468, 1922; see also Hartley, Campbell and Poole, J. Chem. Soc., 93, 428, 1908.

<sup>&</sup>lt;sup>6</sup> Vogel and Jeffery, J. Chem. Soc., 1201, 1931.

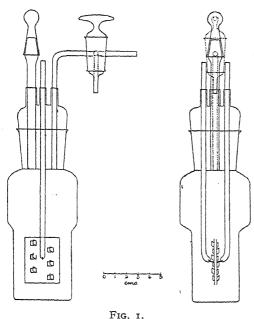
cell for all the others, precautions being taken to avoid absorption of moisture.

The many specimens thus prepared all had the same conductivity (0.0493 × 10<sup>-6</sup> at 50°), but it may be noted here that in a subsequent investigation on the conductivity of other systems containing phenol, a material of lower conductivity (0.021 × 10<sup>-6</sup> at 50°) has been consistently obtained; in fact, it has been found impossible subsequently to prepare any of the higher conductivity material. The phenol was undoubtedly very pure and we are convinced that the higher conductivity cannot be attributed to impurities; addition to the lower conductivity phenol of a number of possible impurities, in quantities far in excess of the total possible contamination of the other material, results in an increase of conductivity negligible in comparison with the difference in conductivity between the two materials. Whether the difference is due to the existence of two different forms of phenol 8 or to tautomerism is a matter for further investigation.

The present measurements are all directly comparable since identical material was used throughout; moreover, the conclusions drawn from them are in no way affected, since measurement of a series of phenol-rich solutions made with the lower conductivity material showed that precisely the same type of curve is obtained, the values gradually merging on the steep portion of the curve.

#### Cell.

The cell used for all the measurements is a modification of that first



employed by Hartley and Barrett 9 and is shown to scale in Fig. 1. The cell itself is made of quartz and the circular crosssection of the top is flattened out below the stopper to a rectangular cross-section, so that the distance between electrodes and the walls is reduced and the rate at which the solution attains the temperature of the thermostat is greatly increased. The electrodes of are platinum (4 cms.  $\times$  3 cms.), coated with grey platinum, and each has six louvres, as shown, to permit free circulation. and thus facilitate mixing of the solution. electrodes are 2 mm.

apart, and are held firmly by small beads of borosilicate glass fused on

<sup>7</sup> Howell and Robinson, about to be published.

<sup>&</sup>lt;sup>8</sup> Tammann, The States of Aggregation, 171, 1926; Z. physik. Chem., 69, 569, 1909; 75, 75, 1910.

<sup>9</sup> J. Chem. Soc., 103, 786, 1913.

at each corner, and the middle of each side. They are provided with stout platinum wires sealed into borosilicate tubes, and contact is made in the usual way through mercury to copper leads. The stopper is also of borosilicate glass ground to fit the cell, and carries not only the electrode tubes but also a wide tube with ground glass stopper through which additions or removals may be made, and a smaller tube bent at right angles and provided with a tap. All these tubes are sealed to the base of the stopper and pass through closely fitting open tubes on the top.

Calculation from the coefficients of expansion of the glass and platinum showed that the cell constant should not vary over the temperature range, and this was verified by determining the conductivity of N/50 potassium chloride, the comparative conductances obtained agreeing

with those interpolated from the published values.10

It was found, however, that the cell constant varied slightly with the volume of solution used. The cell constant was therefore determined with a series of different volumes of N/50 potassium chloride solution and a curve drawn. In the subsequent determinations of the conductivity of the water-phenol mixtures, the volume was in every case calculated from the known weight and density  $^1$  and the corresponding cell constant read from the curve was used for calculation.

#### Solutions.

All solutions were made up by weight in the cell itself. The waterrich solutions were made by adding successive amounts of an 80 per cent. solution of phenol or, for the more concentrated solutions, phenol itself. The phenol was melted in a quartz tube and the approximate amount required was added from a quartz pipette, whilst a stream of air free from carbon dioxide was passed through the cell. The phenol-rich solutions were made by adding water to phenol in a stream of air free from carbon dioxide. The pure water was collected in a quartz flask, and the approximate amount required was blown over into the cell through quartz tubes. After a series of dilutions, when the volume of the solution had become excessive, a portion of the solution was sucked out through a quartz tube by means of a filter pump and the dilution continued. The cell and contents were weighed after each addition both before and after the determination of the conductivity; the loss in weight during measurements was negligible.

Several series of solutions were measured in this way, and the concentrations were so arranged that the end members of one series overlapped those of another, and so gave a check on the extent of contamination

during preparation and measurement.

The time taken by the cell and contents to attain the temperature of the thermostat was considerable—over an hour with the more concentrated solutions. It was reduced as much as possible by frequent shaking, and was readily checked by determining the conductivity at intervals.

At first, the cell was kept closed throughout the measurements at the series of different temperatures, but it was found that occasionally the conductivity would suddenly increase, and this was traced to the ingress through the ground joint of air which carried with it some fouled solution from this region. The difficulty was completely averted by having the

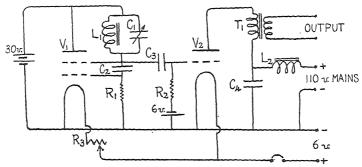
<sup>&</sup>lt;sup>10</sup> Landolt and Bornstein's Tables, 5th edition, 1098, 1923; International Critical Tables, 6, 230 and 234.

cell always open to atmosphere through a small U-tube, one-half (next to the cell) filled with calcium chloride, and the other with soda-lime. The small interchange of air on transferring the cell from one thermostat to another thus took place through this tube; the soda lime removed the carbon dioxide and decomposed the ammonium salts and the calcium chloride absorbed the ammonia.

## The Electrical Assembly.

In order to measure the conductivity of the badly-conducting solutions of this system with the accuracy desired, the electrical arrangements which had to be adopted were unusual in work of this kind.

A true null-point for a network containing resistive and reactive components, when the effective reactance varies with the frequency (as for an electrolytic cell) can be obtained only with alternating current of sine-wave form. An oscillating valve, which can be made to give a sufficiently near approach to a sine-wave, was therefore used as the source of supply. There are many suitable valve arrangements, but



 $V_{\rm l},$  cheap "bigrille" valve.  $V_{\rm l},~\mu=6$  ;  $R_{\rm a}=1500~\omega.$  (Actually four cheap valves in parallel were used.)

L<sub>1</sub> and C<sub>1</sub>, chosen to give frequency desired. (Normally a Sterling I" spark coil secondary and condenser of about ooi mfd., giving a frequency of about 1100, were employed.)

FIG. 2.

one of us possessed a Neuman oscillator, coupled to a small power amplifier, giving about 200 milliwatts output, and this was used. The circuit arrangement and component values are given in Fig. 2. A good waveshape was secured by adjusting the "bigrille" valve to just within its oscillation point by varying its filament resistance  $R_{\rm 3}$ .

The use of telephones as detector is not very convenient, leads to inaccuracies due to their passing currents to earth via the observer's body and limits the precision with which the null-point can be observed by reason of their limited sensitivity.

Instead of telephones, therefore, a valve amplifier <sup>12</sup> and loud-speaker <sup>13</sup> were used. The design of the amplifier is not critical; a large output and a level gain-frequency characteristic are unnecessary. High amplifica-

<sup>&</sup>lt;sup>11</sup> Hall and Adams, J. Amer. Chem. Soc., 41, 1515, 1919; Ulich, Z. physik. Chem., 115, 377, 1925; Woolcock and Murray-Rust, Phil. Mag., vii, 5, 1130, 1928 Lecomte du Noüy, Nature, 127, 441, 1931.

<sup>See Hall and Adams; Lecomte du Noüy, loc. cit.
Howell and Handford, Nature, 127, 522, 1931.</sup> 

tion may therefore be obtained in a small compact arrangement with low current consumption, which is an important consideration, since the amplifier must be fed from batteries and not from the mains. One of us also possessed a three-stage amplifier well adapted to the work, and this was used. The circuit arrangement and component values are given in Fig. 3.

The use of this amplifying detector results in a large increase in sensitivity, but the capacity to earth possessed by it and its associated batteries, though less than that of telephones on an observer's head, still displaces the null-point appreciably. This effect is entirely removed by

using a Wagner earthing device.<sup>14</sup>

For the three arms of the bridge, we used a Tinsley non-inductive resistance box containing a pair of ratio arms and a third arm consisting of five decade dials and a circular slide-wire of total range II,III·I ohms. All of these proved to have residual capacities and inductances so low as to render unnecessary any correction.

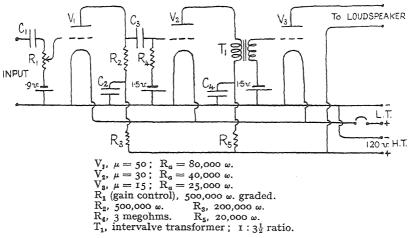


Fig. 3.

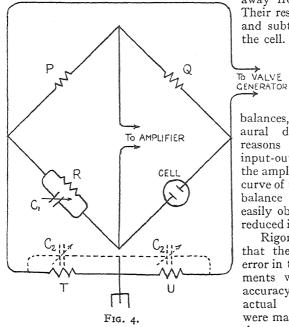
The arrangement of the whole assembly is shown in Fig. 4. P and Q are the non-inductive ratio arms, and R the four dials and slide wire of the Tinsley box.  $C_1$  is a variable condenser of 'OII mfd. maximum capacity and one of 'OOI mfd. maximum capacity in parallel, supplemented when necessary by a bank of ten fixed condensers, each of 'OI mfd. capacity. T and U, which constitute the Wagner earthing branch, are a second pair of ratio arms set to the same ratio as P and Q. The only arms available had appreciable reactive components and the secondary of the oscillator output transformer has capacity to earth. Therefore with bridge ratios other than unity, the refinement was adopted of balancing these out by means of  $C_2$ , a variable condenser of 0.001 mfd., supplemented by a bank of ten 0.001 mfd. fixed condensers.

The bridge components were arranged at a gap in the centre of the row of thermostats. The valve generator was about 20 feet distant, the current being led to the bridge by a twin lead-covered cable whose

<sup>&</sup>lt;sup>14</sup> Wagner, Elek. Z., **32**, 1001, 1911. We were unaware until after the completion of this work that the Wagner earth had been similarly applied by Jones and Josephs, J. Amer. Chem. Soc., **50**, 1049, 1928.

sheathing was earthed. The amplifier and batteries and loud-speaker associated with it were grouped as compactly as possible on a wooden platform away from the bridge and from earthed fittings such as gas and water pipes.

The leads to the electrolytic cell were of twin flexible wire about 10 feet long to enable the most distant thermostats to be reached. They were looped up by curtain-rings to an overhead cord so as to keep them



away from other apparatus. Their resistance was measured and subtracted from that of the cell.

The gain control should preferably be turned to a low value when obtaining preliminary

balances, if only to prevent aural discomfort, but for reasons connected with the input-output characteristic of the amplifier and the response curve of the ear, a preliminary balance is actually more easily obtained with a much reduced input to the amplifier.

Rigorous tests showed that there was no source of error in the electrical arrangements within the limits of accuracy required. When actual cell measurements were made, it was found that these were not quite inde-

pendent of the frequency used. A frequency of about 1100 cycles was adhered to in all the measurements quoted.

It was found impracticable to obtain measurements of the cell resistance to the number of significant figures which the electrical arrangements were capable of giving, chiefly because of the enormous times required for the solutions to become sufficiently constant in temperature, and therefore attain their final resistance values. The choice of apparatus was not regretted, however, since it was extremely easy to use, and enabled readings of the highest accuracy which circumstances permitted to be made with absolute confidence.

# Conductivity-Concentration Relation.

The observed values of the electrical conductivities for all concentrations at each temperature are given in Table I and plotted in Fig. 5. The general form of the curve with its pronounced maximum is typical of the conductivity-concentration curves for concentrated solutions, 15 but there is one feature deserving attention.

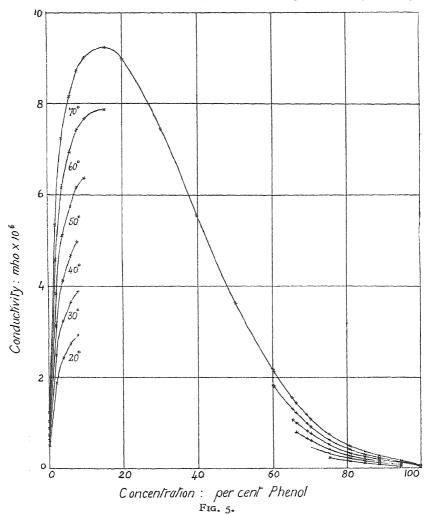
The increase in conductivity on addition of water to phenol is at

<sup>&</sup>lt;sup>15</sup> See, for example, aqueous hydrochloric acid solutions, Howell, J. Chem. Soc., 2843, 1927; water-butyric acid mixtures; Grindley and Bury, ibid., 1005, 1030.

ABLE I

		ı;	4-0107	94 76 547
_	70°.	Calc.	1.20 5.59 7.24 8.24 8.81 1.44 1.19 1.19 1.19 1.19 1.19 1.19 1.1	0.0
	2	Obs.	7.19 7.29 8.15 8.15 8.15 8.13 8.13 8.13 1.15	0.292 0.176 0.0647
	60°.	Calc.	1.04 4.72 6.16 6.95 7.43 7.21 1.21 1.00 0.924 0.634 0.413	0.247 0.150 0.0564
	09	Obs.	1.04 4.72 6.16 6.95 7.43 7.87 7.87 7.82 1.31 1.21 1.21 1.20 0.034 0.415	0.150
	50°.	Cale.	0.891 3.91 5.11 5.76 6.15 0.995 0.766 0.524 0.352 0.365	0.124 0.0493
		Obs.	0.892 3.93 5.11 5.75 6.16 6.36 6.36 0.995 0.766 0.525 0.354	0.203 0.126 0.0493
Conductivity $k \times ro^{6}$ .	40°.	Calc.	0.752 3.169 4.133 4.655 4.978 0.790 0.657 0.285 0.285	0.0994
	40	Obs.	0.752 3.169 4.133 4.655 4.978 0.790 0.657 0.211	0.0995
	30°.	Calc.	0.625 2.492 3.240 3.647 3.903 3.903 0.472 0.221 0.221 0.163	0.0758
	30	Obs.	0.628 2.492 3.230 3.635 3.835 3.835 0.327 0.327 0.221 0.213	0.0757
	20°.	Cale.	0.508 1.879 2.427 2.731 2.929 (0.4108) (0.3370) 0.154 0.157	0.0919 0.0532 (0.03512)
		Obs.	0.508 1.879 2.427 2.731 2.929 0.240 0.154 0.158	0.0532
	Conc. Phenol Per Cent.		2.00 2.00 3.97 6.01 15.36 15.36 20.14 50.18 50.05 60.03 60.03 60.03 60.03 60.03 80.00 80.00 80.80	88.03 94.75 100
	Series No.		A1 A2 A3 A4 A5 A10 A11 A11 A11 A11 A12 A12 A13 A13 A14 A14 A15 A16 A17 A17 A17 A17 A17 A17 A17 A17 A17 A17	B1, D1

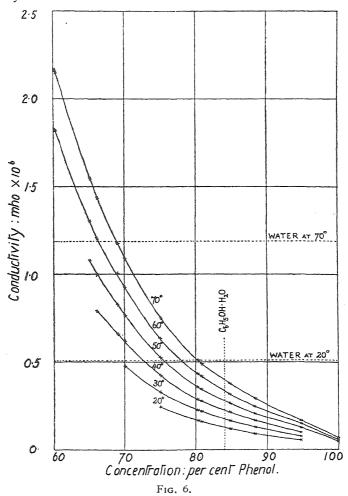
first very small; thus, at 70°, solutions containing up to more than 30 per cent. of water have a lower conductivity than water itself. This is clearly seen from Fig. 6, where the curves for the solutions at the phenol-rich end of the series are shown on a bigger scale. The increase is of a different order of magnitude from that found on addition of phenol to water; thus, at 70°, replacement of 10 per cent. of phenol by



water results in an increase of conductivity which is only one-fortieth of that resulting from replacement of 10 per cent. of water by phenol.

This extremely low conductivity of the phenol-rich solutions is difficult to account for if they are regarded simply as solutions of water in phenol. It cannot be attributed to the low dielectric constant of phenol. Thus, contrasting the system water-butyric acid at 25° with the system water-phenol at 50°, although at these temperatures butyric acid has a lower conductivity  $(0.039 \times 10^{-6})$  than phenol  $(0.0492 \times 10^{-6})$ , the

solution of butyric acid containing 13.83 per cent. of water has a conductivity of  $3.79 \times 10^{-6}$  whereas a solution of phenol containing as much as 15.16 per cent. of water has a conductivity of only  $0.262 \times 10^{-6}$ ; yet the dielectric constant <sup>16</sup> of phenol (9.68 at 48°) is considerably greater than that of butyric acid (2.70 at 17°). The higher viscosity <sup>2</sup> of these phenol-rich solutions is also insufficient to account for their low conductivity.



It has, however, already been suggested that ionisation of waterphenol solutions occurs in two ways.

Addition of phenol to water produces a solution of comparatively high conductivity which, at first, increases with increasing concentration of phenol. The acidic character of these dilute solutions is well known, so that the H or OH is ion is present. There is abundant evidence for

<sup>&</sup>lt;sup>16</sup> Drude, Landolt and Bornstein's Tables, 5th edition, 1039 and 1037 respectively, 1923.

the existence of the OH'3 ion.17 Ionisation, therefore, probably occurs as the result of interaction of solute and solvent in the following manner :- 18

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O' + OH'_3$$
.

Addition of water to phenol, on the other hand, produces a very badly conducting solution. Ionisation perhaps occurs in the alternative manner possible with two hydroxylic compounds:-

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5OH_2 + OH'.$$

There should then be increasing basicity on dilution and one of us (O. R. H.) has endeavoured with Mr. Horrobin to test this point by measurement of the activities of phenol-rich solutions. Unfortunately, it was found impossible to obtain accurate determinations. The quinhydrone electrode was useless, the hydrogen electrode was readily poisoned, and there was a specific effect (perhaps dehydration) with the glass electrode. The readings obtained, however, clearly indicated that there is a definite, though small, increase in pH on addition of water at this end of the series.

As the phenol is progressively displaced by water, combination between the ions will result in the formation of the compound (C<sub>6</sub>H<sub>5</sub>OH'<sub>2</sub>)(OH'), and this should reach a maximum with equi-molecular proportions of water and phenol. Thereafter, with increasing concentration of water, dissociation would occur in aqueous solution, and it is clearly seen from Figs. 5 and 6 that only after this point does the conductivity begin to rise rapidly.

The basic character of phenol and the formation of compounds is shown in its reaction with phosphoric acid 19 yielding C<sub>6</sub>H<sub>5</sub>OH. H<sub>3</sub>PO<sub>4</sub>, which, indeed, the discoverers regard as an oxonium compound; with oxalic acid 20 yielding C<sub>6</sub>H<sub>5</sub>OH. (COOH)<sub>2</sub>; with sulphuric acid 21 yielding 2C<sub>6</sub>H<sub>5</sub>OH . H<sub>2</sub>SO<sub>4</sub>; and with trichloracetic acid <sup>22</sup> yielding

Compounds of uncertain composition are also found with sulphur dioxide 23 and carbon dioxide.24

It would be of interest to investigate the effect of substitution on this characteristic of phenol. Thus p-cresol should be more basic and p-chlor-phenol less basic than phenol. It is noteworthy that p-cresol forms compounds with phosphoric acid, sulphuric acid and trichloracetic acid of similar composition to those obtained with phenol.

## Conductivity-Temperature Relation.

The electrical conductivities observed for each concentration are plotted against the temperature in Fig. 7.

<sup>17</sup> Goldschmidt and Udby, Z. physik. Chem., **60**, 728, 1907; Lapworth and Fitzgerald, J. Chem. Soc., **93**, 2163, 1908; Lapworth, ibid., 2187; Hantzsch. Z. Elektrochem., **29**, 221, 1923; ibid., **30**, 194, 1924; Ber., **58**, 941, 1925; Volmer.

Ann., 440, 200, 1924.

18 Compare Kendall, Booge and Andrews, J. Amer. Chem. Soc., 39, 2302, 1917; Kendall and Booge, *ibid.*, 2323.

19 Hoogwerff and van Dorp, *Rec. Chem. Trav.*, 21, 349, 1902.

20 Schmidlin and Lang, *Ber.*, 45, 908, 1912.

21 Kendall and Carpenter, *J. Amer. Chem. Soc.*, 36, 2498.

Kendall, *ibid.*, 38, 1309.
 Holzer, J. pr. Chem., 25, 463, 1882.

<sup>24</sup> Barth, Ann., 148, 49, 1868; Klepl, J. pr. Chem., 25, 464, 1882.

It is seen that all the curves are smooth. Each is expressed by the equation

$$\kappa_{t^{\circ}} = \kappa_{20^{\circ}} + \alpha\theta + \beta\theta^{2},$$

where  $\alpha$  and  $\beta$  are constants having different values for the different concentrations and  $\theta$  is (t-20). The conductivities calculated from the equation are given in Table I, and it is seen that, in view of the difficulties

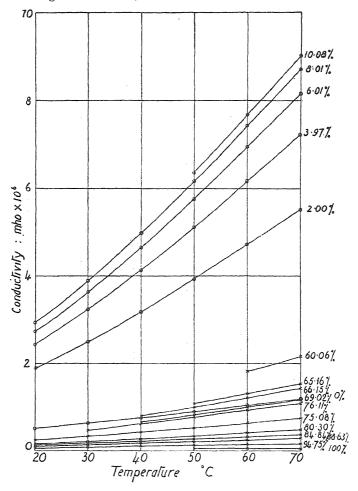


Fig. 7.

of making measurements over such a wide range of temperature, the agreement between the observed and calculated values is satisfactory.

The values of  $\alpha$  and  $\beta$  are given in Table II, and plotted against the concentration in Fig. 8, where it is seen that the curve exhibits a distinct inflexion. The concentration at which this occurs cannot be determined exactly, but it is at about equi-molecular proportions of water and phenol. It will be recalled that the curve of one of the constants in the density-temperature relation plotted against the concentration showed

TABLE II.

	Water-rich Soluti	ons,	Phenol-rich Solutions.			
Cone. Per Cent.	$\alpha \times 10^3$ .	β× 10 <sup>5</sup> .	Conc. Per Cent.	α × 103,	β× 10 <sup>5</sup> .	
0 2-00 3-97 6-01 8-01	11·1 58·1 77·2 86·9 92·4	5·5 32·0 40·5 46·4 50·5	66·15 69·02 70·11 75·08 80·30 80·80 84·84 88·63 94·75	17·85 14·51 13·07 8·31 5·44 5·28 4·26 3·16 2·21 0·29	5.44 4.68 4.04 3.82 3.12 2.80 1.84 1.76 0.51 0.60	

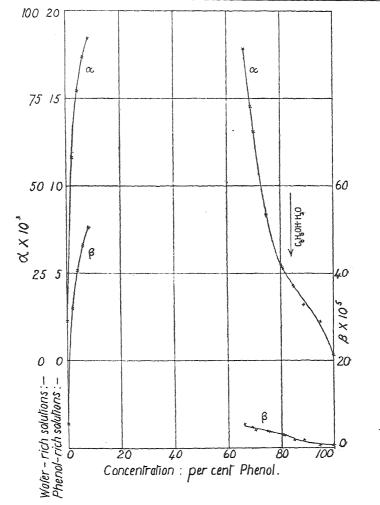


Fig. 8.

a marked inflexion, and that of the viscosity-temperature relation a sharp minimum at this point. There is therefore very strong evidence of a definite association between water and phenol in equi-molecular proportions.

## Summary.

I. The electrical conductivities of a series of solutions of water and phenol of different concentrations, suitably spaced over the whole range of miscibility, have been measured at 20°, 30°, 40°, 50°, 60° and 70°.

2. A very sensitive arrangement embodying the "Wagner earth" and employing a loud-speaker for the determination of electrical conductivities

is described.

- 3. A still for the preparation of conductivity water and a cell suitable for determining the conductivity of badly-conducting solutions at a series of temperatures are described.
- 4. The form of the conductivity-concentration curves is discussed.
  5. The conductivity-temperature curve for each concentration is smooth and represented by the equation

$$\kappa_{t^{\circ}} = \kappa_{20^{\circ}} + \alpha(t-20) + \beta(t-20)^{2}.$$

- 6. The curves of the constants  $\alpha$  and  $\beta$  against the concentration (like those of the density-temperature and viscosity-temperature relations) exhibit inflexion at a concentration corresponding to equi-molecular proportions of water and phenol.
- 7. The association of water and phenol in equi-molecular proportions is explained by the dual dissociation of phenol

$$C_6H_5OH_2^* + OH' \rightleftharpoons C_6H_5OH + H_2O \rightleftharpoons C_6H_5O' + OH_3^*$$

and formation of the compound (C<sub>6</sub>H<sub>5</sub>OH<sup>\*</sup><sub>2</sub>)(OH').

The College of Technology, Manchester.

# THE THERMAL DECOMPOSITION OF CRYSTALS OF BARIUM AZIDE.

By F. E. HARVEY, PH.D.

Received 17th March, 1933.

Crystals of barium azide, BaN6. H2O, lose their water of crystallisation when kept at room temperature, giving a white pseudomorph. These dehydrated crystals decompose at a measurable rate at temperatures above 95° C., liberating nitrogen and metallic barium. pressure-time curves obtained for the reaction are similar in character to those of mercury fulminate.<sup>1</sup> There is an induction period the length of which decreases with increasing temperature and a period of acceleration of the reaction which obeys the law

$$\log (dp/dt - dp_0/dt) = k_1 t + const., \quad . \quad . \quad . \quad .$$

previously found to hold for the decomposition of fulminate.

<sup>1</sup> Farmer, J.C.S., 121, 174, 1922; Garner and Hailes, Proc. Rov. Soc., 139A, 576, 1933.

## Experimental.

The experimental technique has been described in previous papers, and since very few modifications have been made in the methods employed, it is unnecessary to describe it in detail.

Barium azide obtained from the General Electric Company was crystallised from water and crystals of good shape, 1-4 mg. in weight, selected. A single crystal of known weight was suspended in a platinum bucket in the apparatus outlined in Fig. 2,2 and a small platinum disc was placed over the crystal at the bottom of the bucket. The bucket was suspended in a cold part of the apparatus while the reaction vessel was being evacuated. After evacuation for 24 hours, the crystal was lowered into the reaction vessel and periodical pressure measurements taken on a McLeod gauge. The volume of the apparatus, calibrated with dry air from a small mercury weight pipette fused in the side of the apparatus, was approximately 3000 c.c. At 128° C., the volume calculated from the equation  $v = p_1/p_2$ , where  $p_2$  is the pressure in the apparatus and  $p_1$  the pressure of the same amount of gas when occupying I c.c., ranged from 3110 to 3140 c.c. between  $2-7 \times 10^{-3}$ . The drift in the values between these pressures was probably due partly to thermal diffusion and partly to adsorption.

The amount of nitrogen liberated from a single crystal 1-2 mg. in weight was found to be 98.5 per cent. of that calculated from the weight of azide taken (the mean of six experiments).

### Results.

Typical pressure-time curves are given in Fig. 1 (I and A). These show an induction period over which there was an approximately linear rate of evolution of gas,  $2.5 \times 10^{-7}$  cm. per min., which includes gas liberated from the walls of the reaction vessel. This gives  $dp_0/dt$  in equation I. At the end of the induction period the acceleration of the reaction occurs according to equation I (see Fig. I (II.)). The exponential law only holds for about I/10 of the total decomposition. This period is shorter than for fulminate crystals, and much shorter than for ground fulminate and lead styphnate. In the last two cases the law holds up to the time of half decomposition. The acceleration is sometimes terminated by a change of slope (at A), after which for a brief period the rate is approximately constant. For the last 20 per cent. of the decomposition the unimolecular law is obeyed.

The experiments were carried out over the range of temperature 100-130° C., over which range a black crystalline residue was obtained. Some work was done at higher temperatures with a Pirani gauge which showed that it was difficult to cause the crystals to detonate. Above 140° C., the reaction was sometimes sufficiently violent to blow the disc out of the bucket and on these occasions no pseudomorph was left behind. Thus the process which occurred may correspond to the first stages of detonation.

Centres of Decomposition.—If partially decomposed crystals be removed from the apparatus during the period of acceleration of the reaction, and examined under the microscope, it is seen that centres of decomposition have been formed consisting of metallic barium (Fig. 2). These, which occur both on the surface and throughout the mass, have

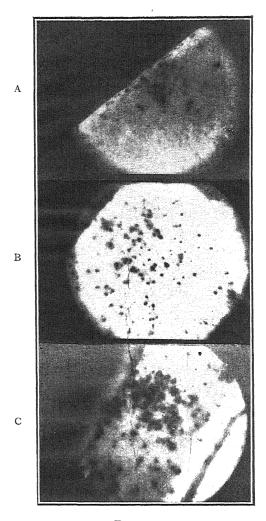
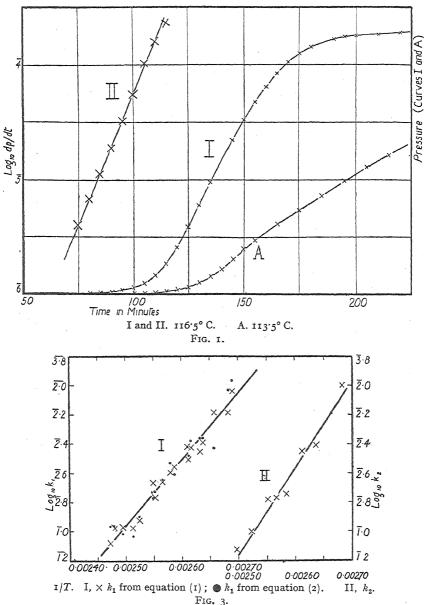


Fig. 2. A. Group of centres near edge of crystal. C. Centres touching towards end of period of acceleration. [To face page 654.



an irregular shape, and in a few cases a ring structure. On standing in the air the barium oxidises, and towards the end of the oxidation is present as a ring corresponding with the external boundary of the original centre.



The distribution of the centres over the surface is unusual. They are grouped in clusters on the surface in a manner not determined by a probability law. This indicates either that the surface does not possess

uniform properties all over, or that the centres are formed from one another. The number of the centres in unit volume is not so high within the crystal as on the external surface. Nor are those inside the crystal as large as those formed on the external surface. In consequence of this, the centres on the surface begin to touch one another long before the reaction is complete. This possibly accounts for the change of slope

The number of centres and their size increases with time. Attempts were made to count these centres and to determine the manner in which their number increased throughout the reaction, but it was found that for crystals of the same batch, heated at the same temperature for the same length of time, the numbers obtained were not reproducible. This is very probably the cause of the variations observed in the velocity of the reaction in the crystal (see later). In one experiment at 100.5° C., a crystal of about 2 mg., when removed from the apparatus after heating for 330 minutes, gave approximately 1000 centres visible on the surface. This is in marked contrast with the behaviour of crystals of mercury fulminate which on heating become browned throughout, without showing any marked structure under the microscope.

The matrix in which the centres are embedded does not undergo any visible change of colour or appearance on heating, so that it is probable that the formation of centres is the only chemical change that occurs, although the lack of reproducibility in the number of centres makes it impossible to ascertain this with any certainty.

## Velocity Constants of the Reaction.

The early stages of the reaction after the induction period are governed by the equation

$$dp/dt = kp, \quad . \qquad . \qquad . \qquad . \tag{2}$$

which on integration, gives

$$\log_{10} p = kt/2.303 + \log_{10} p_0.$$
 (3)

Here  $\log_{10} p_0$  is a constant independent of temperature within experimental error, and has the average value 9.87 (log. cm. Hg). From equations (2) and (3) it follows that

$$\log_{10} dp/dt = kt/2 \cdot 303 + \log_{10} k + \log_{10} p_0. \qquad . \tag{4}$$

This equation is also in agreement with the facts, and the experimental values of  $\log_{10} (kp_0)$  given in the table agree with those calculated from equations (2) and (3) within experimental error.

Consequently, there are several ways in which the experimental results may be tabulated. Equation (4) has been employed as a basis for calculations, since this was the equation used in the earlier paper on fulminate, and also since it appeared to be the most important equation of the three. In the following table is given the temperature of the experiment, the weight of the crystal in mg., the length of the induction period in minutes, the time when  $\log_{10} dp/dt = 10^{-5}$  cm./min., k/2.303from equation (4), k/2.303 from the equation dp/dt = kp, the constant from equation (I) and the velocity constant of the unimolecular reaction calculated from equation

$$k_2 = \frac{1}{t} \log_{10} \frac{p_f}{p_f - p_t}$$
 (5)

All	rates	s have	beer	n c	alculated	in	cm./min.	With	the	aid	of	these
lata	i, it	is pos	sible	to	reproduce	the	e experime	ental o	urve	s.		

T° C.	Wt. in mg.	Induction Period. min.	Time log rate = 5 min.	$\begin{array}{c c} k_1 \\ \hline 2 \cdot 303 \\ \text{Equation} \\ (4) \cdot \end{array}$	$\begin{array}{c} k_1 \\ 2 \cdot 303 \\ \text{Equation} \\ (5). \end{array}$	Const. Equation	$k_2$ .
98·9 100·2 103·1 106·6 107·0 109·0 109·8 110 113·5 114·6 116·5 118·8	1·521 2·128 0·930 2·187 1·83 2·032 1·461 1·716 1·003 1·72 0·76 2·705 1·425	340 270 245 150 130 115 120 90 90 60 60	520 399 287 212·5 178 166 147 173 113 109·5 84 65·5	0.0108 0.0151 0.0151 0.0246 0.0281 0.0266 0.0320 0.0262 0.0361 0.0390 0.0457 0.0584 0.0462	0.0091 0.0107 0.027 0.0229 0.0229 0.0240 0.0302 0.0263 0.0407 0.0339 0.0447 0.0537 0.0589	TT·500 TT·000 Tō·60 Tō·15 Tō·62 Tō·20 Tō·50 Tō·92 Tō·92 Tō·94 	0·0099 0·0253 
123·2 125·0 128·1 130·1 131·7	2·095 4·125 1·28 1·574 0·86	30 25 20 20	47 35 28·5 26·5 22·5	0.0848 0.0962 0.0949 0.0948 0.1219	0.080 0.110 0.105 0.093	9.50 9.50 8.26 8.48 8.26	0·135

# Temperature Coefficient of the Reaction.

The velocity constants of the reaction,  $k_1$  and  $k_2$ , are dependent on the temperature and the graphs of  $\log_{10}$  constant against 1/T give straight lines (Fig. 3) from which the critical increments of the reaction may be calculated. Those for  $k_1$  and  $k_2$  are of the same order, being  $21 \cdot 1$  and 27 K. cal. respectively. The constant, equation (1), is also dependent on the temperature and its critical increment is larger than either of the above. The errors which occur in the determination of the constant are too large to make it worth while quoting the actual figure.

#### Discussion.

The decomposition of barium azide is associated with the formation of a relatively small number of centres visible under the microscope. An attempt was therefore made to explain the acceleration of the reaction in terms of the growth of the interface between the barium nuclei and the azide. The growth of the nuclei can be considered in terms of two hypotheses: (I) the number of the nuclei is constant from the beginning to the end of the reaction,\* that is, they are all formed on introduction of the crystal into the reaction vessel; and (2) the nuclei are the result of thermal activation and are formed at an approximately constant rate, viz,  $N_0$  per minute. According to the first hypothesis, since the nuclei all start at the same time, their external areas will be equal in magnitude, so that the total area of the interface will be proportional to  $m^{2/3}$ , where m is the mass decomposed, or  $dp/dt = kp^{2/3}$ . Since in solid reactions the rate of penetration of the interface into the solid is usually found to be

<sup>\*</sup> This is actually in disagreement with observation, for the number of centres definitely increases with time.

constant, it is possible that the rate of reaction would be found proportional to  $t^2$ . The second hypothesis leads to the equation,

$$dp/dt = k(1 + 2^2 + 3^2 + 4^2 \dots t^2) = k(2t^3 + t^2 + 2t + 1),$$

or for long times such as are found in the present experiments,  $dp/dt = kt^3$ . Actually, the experiments show that dp/dt = kp, and that the rate increases approximately as the tenth power of the time \* instead of the square or the cube of the time as expected from hypotheses (I) and (2), so that neither hypothesis is in agreement with the experimental facts. The difficulties of applying the usual conceptions of the rate of growth of centres to the decomposition of barium azide seem to be insuperable.

A branching mechanism of some kind is indicated. This could be of the type postulated in an earlier paper, according to which the reaction spreads throughout the mass of the solid by means of branching chains which possess a spatial character. These chains were assumed to branch according to the expression,  $dN = (N_0 + kN)dt$ , where  $N_0$  is the number of chains started per minute, and N the number of branches in existence at any time, k being a branching coefficient. This leads to the expression found,  $\log (dp/dt - a) = k_1 t + const$ . The objection to this view lies in the fact that very substantial nuclei of metallic barium are formed instead of the metallic cloud predicted by the above mechanism. If this hypothesis were correct, then the crystal should darken gradually throughout the mass, as was observed for fulminate.

It is hoped that further work on the action of  $\beta$  and  $\gamma$  radiation on barium azide crystals  $^3$  will lead to the elucidation of some of the above difficulties in the interpretation of the experimental results.

#### Summary.

The thermal decomposition of single crystals of dehydrated barium azide has been studied between the temperatures 100-130° C. An induction period is observed which is similar to that found for mercury fulminate. The reaction accelerates at a rate which increases as the tenth power of the time and the acceleration obeys the law,  $\log (dp/dt - a) = k_1t + const.$  previously found to hold for fulminate and lead styphnate. Towards the end of the reaction, the unimolecular law is obeyed.

Nuclei of metallic barium are produced both on the surface and in the interior of the crystal.

I wish to express my thanks for a grant from Imperial Chemical Industries, Ltd., which has defrayed the cost of the apparatus employed in the research.

\* The plot of  $\log dp/dt$  against  $\log t$  for the period of acceleration gives a slightly curved in of which the slope is approximately 10.

<sup>3</sup> Cf. Nature, 1933, 131, 513.

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# STUDIES IN THE SPONTANEOUS OXIDATION OF ZINC AND THE NATURE OF "PYROPHORIC" ZINC.

By W. S. Sebborn, B.Sc., A.I.C.

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By "pyrophoric" zinc it is proposed to indicate zinc which undergoes spontaneous oxidation in air, with incandescence. It has often been observed that, when large masses of zinc dust have been used in reduction reactions, and then left in a damp state after separation from the other reagents, they become hot and oxidise, and may even be a source of fire: but no investigation of this phenomenon appears to have been recorded.

Zinc sponge prepared by electrolysis has been known for many years, and it has been found that spongy zinc deposits, obtained under certain conditions, exhibit "pyrophoric" properties on drying. Zinc dust prepared by drying zinc sponge has been described, and the product used commercially: but although mention has been made of the tendency of such zinc dust to oxidise, when prepared under certain conditions, the matter does not appear to have undergone fuller investigation.

The following paper describes experiments which have been carried out in investigation of the spontaneous oxidation of zinc, and of the conditions for the zinc to become "pyrophoric" or to oxidise spontaneously with incandescence.

# Experimental.

# Experiments with Finely Divided Zinc, prepared Electrolytically.

Zinc was deposited in a spongy condition by the electrolysis of solutions of various zinc salts, under conditions of low metal ion content and high current density, as described by previous workers.<sup>3</sup> At the conclusion of the electrolysis, the non-adherent spongy deposit was removed from the cathode, by means of a glass rod, to a watch-glass.

The electrolytes considered comprised the following: zinc sulphate; zinc chloride (each in aqueous solution at concentrations between 0.5 per cent. and 5 per cent.); zinc nitrate; dilute solutions of zinc oxide in excess ammonium hydroxide solution; solutions of zinc hydroxide in sodium hydroxide formed by adding excess sodium hydroxide to zinc sulphate solutions; solutions of zinc hydroxide in ammonium hydroxide formed by adding excess ammonium hydroxide to zinc sulphate solutions; zinc sulphate solutions containing sodium sulphate; zinc sulphate solutions containing ammonium sulphate. Electrolysis was carried out in still

381, 1900.

<sup>2</sup> D.R.P., 276984, 3/5/13; Patentschrift 282234, 1/10/20; Chemische Fabrik

<sup>3</sup> Morgan and Ralston, Trans. Amer. Electrochem. Soc., 30, 220, 1916.

<sup>&</sup>lt;sup>1</sup> Mylius and Fromm, Z. anorg. Chem., 9, 164, 1895; Foerster and Gunther, Z. Elektrochem., 5, 20, 1898; 6, 301, 1899; L. Glaser, Z. Elektrochem., 7, 368 and 381, 1900.

solutions, using a vertical anode and cathode, of electrolytic rolled sheet zinc.

The deposits obtained as described above were in each case divided

into three portions.

Excess electrolyte was removed from one portion of the deposit, by pressing it between filter papers; the slightly damp mass thus obtained was left exposed to the air on a watch glass for a few minutes, and was kept under observation. In all cases where the deposit had been obtained from solutions containing either sodium hydroxide or sodium salts likely to yield sodium hydroxide by electrolysis at the high current densities employed, in the absence of agitation, the damp mass was observed to get hot very rapidly, vigorous oxidation accompanied by incandescence finally occurring at the end of a few minutes.

The deposits obtained from the solutions of zinc salts free from sodium ions, and also from those containing ammonium ions, when examined under these conditions, did not exhibit this phenomenon of vigorous rapid oxidation, but oxidised only very slowly, with no appreciable rise

in temperature.

The second portion of the deposit was transferred to a beaker, and was washed several times, by decantation, with distilled water, until free from adhering electrolyte; the surplus water was removed by pressing between filter paper and the damp mass exposed to the air on a watch-glass, as before. Under these conditions, it was found that in no case did spontaneous oxidation of the deposits occur, nor was any noticeable rise in temperature observed. Upon subsequently moistening with a few drops of 10 per cent. sodium hydroxide solution, vigorous and rapid oxidation, accompanied by incandescence, was observed in each case.

The remainder of the deposit was washed free from electrolyte by decantation with distilled water, followed by a final wash with alcohol and ether. It was then transferred to a Gooch crucible, sucked dry, and finally dried in an oven at 90° C. The nature of the deposit was found to be such as to permit the use of a Gooch crucible without the customary filter mat of asbestos or similar material, hence contamination of the deposit by foreign matter was avoided. The dried residue thus obtained was found to be a very fine powder, and, in the dry state, was very stable under ordinary atmospheric conditions; when heated on a crucible lid, it readily ignited, and burned with a brilliant bluish flame. On being moistened with a few drops of 10 per cent. sodium hydroxide solution, considerable heat was evolved, and vigorous oxidation, with incandescence, took place. Potassium hydroxide solution produced the same effect, but when sodium carbonate and potassium carbonate solutions were used, the phenomenon was not observed, nor did noticeable oxidation occur when ammonium hydroxide was used. Moistening with concentrated solutions of ammonium chloride produced no result, but it was found that when the deposit, moistened with ammonium chloride solution, was heated on a crucible lid, it did not ignite, but melted, to form small globules of metallic zinc. Dilute acids were then tried, but moistening the deposit with these resulted only in evolution of hydrogen.

A quantity of the deposit was next taken and excess water added to produce a suspension. The mixture was transferred to a test tube, and saturated with nitrogen gas. A few drops of 10 per cent. sodium hydroxide solution were added, and the mixture was evaporated to dryness in the test tube, warm dry nitrogen being passed through the

tube until all moisture was expelled. No incandescence took place, even after the dried mass was transferred into the air and moistened with water. The sodium hydroxide originally added appeared to have been transformed into sodium zincate, which was, however, not peptised by the water added. On moistening the mass with a few drops of 10 per cent. sodium hydroxide solution, however, and removing excess moisture by means of filter paper, the mass became very hot, and oxidised rapidly.

# Experiments with Zinc Dust.

To Render Zinc Dust "Pyrophoric."—About 50 grams of zinc dust, of the quality used for laboratory reductions, was moistened with 10 per cent. sodium hydroxide solution, and thoroughly mixed to form a stiff paste. Excess moisture was then removed by pressing between filter papers. The mass was then placed on a sheet of asbestos board, and exposed to the air of the laboratory. After about ten minutes steam began to rise rapidly, and after fifteen minutes the mass commenced to glow brightly, with vigorous oxidation, the incandescence spreading rapidly. The experiment was repeated, using different samples of zinc dust, and a positive result was obtained each time.

**Experiments in Inert Atmosphere.**—The experiments which were carried out in an inert atmosphere, as described above, were repeated, with commercial zinc dust in place of the electrolytic zinc. Similar results were obtained, but the reaction was not quite so vigorous as when

the more finely divided electrolytic material was employed.

The Solubility of Zinc Oxide and Zinc Dust in 10 Per Cent. Aqueous Sodium Hydroxide Solution.—Five grams each of zinc oxide (British Drug Houses A.R. Quality) before and after ignition for 1 hour over a blast, and commercial zinc dust, were separately shaken vigorously with 50 c.c. of 10 per cent. sodium hydroxide solution, at the temperature of the laboratory. In each case the suspension was filtered, and zinc was determined in the filtrate by titration with potassium ferrocyanide in the usual manner. The amounts dissolved are shown in the table. When zinc dust was employed, no visible evolution of hydrogen was observed.

Zinc content of filtrate (expressed as Zn).

0.445 grams.

0·425 ,, 0·125 ,,

Zinc oxide (before ignition)
Zinc oxide (after ignition)
Zinc Dust

The content of metallic zinc in the zinc dust was estimated in the usual manner, by measurement of the amount of hydrogen evolved from a weighed sample, when treated with dilute acid under standard conditions. The zinc dust was found to contain 94.7 per cent. metallic zinc, the remainder being composed of oxide, hydroxide, and basic carbonate of zinc.

It thus appears that treatment of zinc dust with 10 per cent. sodium hydroxide solution, in the cold, results in solution of the oxide, etc., present, and not of the metal: and that 100 c.c. of 10 per cent. sodium hydroxide solution at room temperature is capable of dissolving about 1 gram of zinc oxide. Special experiments showed that when an excess of sodium hydroxide solution is taken, the whole of the zinc oxide dissolves in the cold.

# The Effect of Moistening Various Finely Divided Metals with 10 Per Cent Sodium Hydroxide Solution.

The metals cadmium, lead, and copper were obtained in a finely divided state by the employment of similar methods to those used for the electrolytic preparation of zinc dust; spongy deposits of the metals were obtained by electrolysing dilute solutions of suitable salts, the resulting sponge being washed with water, alcohol and ether successively, sucked dry in a Gooch crucible and finally dried at 85° C. The dried powder was moistened with 10 per cent. sodium hydroxide solution, excess moisture being removed by pressing between filter papers. In the case of copper and lead, no reaction was observed; cadmium so treated, however, grew hot and darkened somewhat in colour, but could not be made to glow.

It was not found possible to prepare finely divided aluminium by electrolysis: but when commercial aluminium powder, previously freed from oil by washing in benzene, was moistened with even very dilute sodium hydroxide solution, visible and rapid evolution of hydrogen

occurred, but no incandescence.

#### Observations and Deductions.

- (I) When finely divided zinc, either the ordinary zinc dust of commerce, or that prepared electrolytically, is moistened with 10 per cent. sodium or potassium hydroxide solution, in the presence of air or oxygen, the excess moisture being removed by expression, a reaction takes place, considerable heat is evolved, and the metal is oxidised to zinc oxide with incandescence.
- (2) This phenomenon is not observed when the operation takes place in an inert atmosphere (nitrogen) or when solvents for zinc oxide and hydroxide other than potassium or sodium hydroxides are employed (dilute acids, ammonium hydroxide, ammonium chloride).

(3) The presence of a small amount of sodium or potassium hydroxide,

moisture, and oxygen is essential for the reaction to take place.

(4) The mechanism of the reaction appears to be as follows: Sodium and potassium hydroxides dissolve the surface film of oxide and hydroxide from the metallic zinc forming the respective sodium and potassium zincates. The combined effects of the heat of this reaction and the removal of the protecting oxide film from the naturally reactive zinc cause further oxidation to take place: the resultant new oxide film is again removed by the caustic alkali, hence the reaction  $Zn+O \rightarrow ZnO$ proceeds with acceleration, until the temperature is sufficient to cause incandescence.

As regards other solvents for zinc oxide, dilute acids also attack the metal, liberating hydrogen, which protects the metal from oxidation, while in the case of ammonia and its salts, gaseous ammonia is always present, again protecting the metal from oxidation by acting as an inert atmosphere.

With cadmium, the reaction takes place with much less vigour. This is probably due to the smaller affinity of cadmium for oxygen, and to the fact that cadmium oxide is not attacked by alkalis to the same extent as is zinc oxide, sodium cadmiate being formed only by solution of cadmium oxide in molten sodium hydroxide.4 With aluminium, no effects such as those described were observed, in spite of its greater

<sup>&</sup>lt;sup>4</sup> J. W. Mellor, Theoretical and Inorganic Chemistry, Vol. IV, p. 530.

affinity for oxygen. In this case the hydrogen liberated by the reaction of the sodium hydroxide solution with the metal most probably protects it from oxidation.

In conclusion, the author wishes to express his thanks to Dr. H. Sand, at whose suggestion this investigation was undertaken, for his interest and advice during its progress.

The Sir John Cass Technical Institute, London, E.C.

# REVIEWS OF BOOKS.

Lehrbuch der Physikalischen Chemie. By Dr. Karl Jellinek, Professor in the Technischen Hochschule, Danzig. (Stuttgart: Ferdinand Enke. Vol. IV. (completion). Pp. xiv + 266 with 194 diagrams. Price 26 R.M., unbound.)

The final section of Vol. IV. of this textbook is a continuation of the earlier section on the laws of concentrated solutions and in particular of the laws governing solid solutions. The main part of this section is, however, devoted to the Phase Rule, as applied to one, two, three and four component systems. The treatment is comprehensive and the thermodynamical aspect is stressed wherever possible. A full account is given of the various types of systems met with in the application of the phase rule, and the phase diagrams are very carefully described and their quantitative meaning made clear. The author does not, however, refer in any detail to the experimental side of the subject and does not show how the application of the X-ray analysis has thrown light on the phase diagrams. The treatment is entirely theoretical.

The section is a very valuable addition to the textbook, and should prove very useful as a work of reference.

W. E. G.

Ternäre Systeme. Elementare Einfuhrung in die Theorie der Dreistofflegierungen. By Dr. G. MASING. (Leipzig: Akademische Verlagsgesellschaft., M.B.H., 1933. Pp. viii + 164 and 166 diagrams. Price 8.30 R.M., unbound.)

The literature on ternary systems is very widely scattered and has not hitherto been summarised in a simple manner in textbook form. As a consequence, the general knowledge of ternary systems is limited to the few special cases which are briefly described in general textbooks on the phase rule. The presentation of ternary systems in such textbooks is usually very brief and is sometimes misleading because of omissions of relevant detail. Even the simplest ternary diagram, such as that of bismuth, tin and lead, is usually incomplete, only the melting-point surfaces being given, and the three- and four-phase systems being almost completely ignored. The author seeks to remedy this state of affairs by an elementary review of the general principles and methods of classification employed in the study of ternary systems.

The author discusses in detail seven types of systems which are fully described with the aid of numerous diagrams of space models and cross sections.

To anyone who is well acquainted with the vagaries of two component systems, even a brief examination of these diagrams gives a vast amount of information. In addition, three special cases, iron—silicon—aluminium, tin—zinc—copper, and the ternary systems of iron, are described in the last three chapters of the book.

In view of the increasing industrial importance of the ternary systems, the book by Dr. Masing is very opportune and should prove of considerable value both to those desiring a bird's eye view of the subject and to those who are working in this field.

W. E. G.

Bandenspektren. (Handbuch der Experimental-physik, Ergänzungsband I.) Von W. WEIZEL. Pp. xi + 461. Leipzig, Akademische Verlagsgesellschaft, 1931. Price, Brosch. 43 M., Geb. 45 M.

This book may truly be described as the most comprehensive and authoritative volume yet produced on band spectra. The author has made an exhaustive study of the band spectra of diatomic molecules, and his references to experimental work seem to be complete as far as it has been possible to test them. He combines an encyclopædic knowledge of the experimental facts with a clear understanding of the theoretical principles involved, and the result is a book which is remarkable for its clear and logical development.

The first chapter is devoted to an account of the theory of elections in a field of two centres, from which the nomenclature and symmetry properties of the spectral terms of diatomic molecules are derived. This leads to a discussion of many important properties of diatomic molecules such as the conditions for dissociation and predissociation. The text here, as elsewhere throughout the book, is profusely and admirably illustrated. In the second chapter the probability of transitions between different states is worked out on quantum mechanical principles and numerous selection rules are derived for transitions between states of different parity and symmetry as well as between rotational, vibrational, and electronic states.

The second half of the book is devoted to a comprehensive survey of the known experimental facts concerning the spectra of diatomic molecules. It is enriched by an extensive bibliography, which will be invaluable for purposes of reference to all workers in this field, whether experimental or theoretical.

The author gives no account of infra red or fluorescence or Raman spectra, but this is probably not a disadvantage as these subjects have been fully dealt with elsewhere, and their omission gives the author more scope for the subject in which he has himself specialised. He might, however, with advantage have included more photographs of typical spectra.

The text is admirably printed and worthily maintains the high standard set in the earlier parts of the Handbuch.

J. E. L.-J.

# STUDIES ON ADSORPTION — PART V. — THE SORPTION OF VAPOURS BY ACTIVATED CHARCOAL.

By L. J. Burrage.

Received 11th April, 1933.

In previous work  $^1$  it had been deduced that water vapour was partly adsorbed by the  $C_X O_Y$  complex which existed on the charcoal surface, and from further work  $^2$  it appeared that the presence of this complex tended to cause the isothermal to "sweep-over" at a lower pressure than would be the case if the pores were quite free from  $C_X O_Y$ . By employing the flushing-out technique  $^3$  it was found possible to remove this oxygen compound, equilibrium then being instantaneous or almost so.

As a result of this work it was decided in this experiment to build up as much  $C_{\mathbf{X}}O_{\mathbf{Y}}$  on the surface as was possible and then carry out a sorption and desorption isothermal with water. Finally the charcoal was to be flushed out and a further desorption isothermal determined, the whole experiment to be carried out at 25° C.

# Experimental.

The apparatus employed and general procedure were the same as described in previous publications.3,4 Charcoal A 5 was chosen for this investigation since it formed a large quantity of the C<sub>X</sub>O<sub>Y</sub> complex, as was shown by the large amount of drift observed with a CCl4 isothermal after 800° evacuation. The charcoal was evacuated to zero pressure at 110° in the usual manner, to remove as much adsorbed material as possible, and allowed to stand in contact with dry oxygen at atmospheric pressure for 50 hours, when it was re-evacuated to zero pressure at room temperature. A sorption isothermal was then carried out, the pressures of the evolved O2 and CO2 being noted. The analysis was carried out in the following manner. The freezer was surrounded with liquid air, CO, and H<sub>2</sub>O being frozen out, thus giving the pressure of permanent gas—O<sub>2</sub> in this case. This was pumped away and the CO<sub>2</sub> and H<sub>2</sub>O allowed to vaporise. The freezer was next surrounded with melting methylcyclohexane, the water being frozen out and the CO<sub>2</sub> remaining in the vapour phase. It was realised that this CO<sub>2</sub> pressure would not be quite correct since some CO<sub>2</sub> will be frozen out in the ice. As it was not known whether this amount was large or small, the whole of the water vapour outside the container was pumped away after each point to ensure that no CO<sub>2</sub> which had been freed from the charcoal surface

<sup>&</sup>lt;sup>1</sup> Trans. Faraday Soc., 29, 458, 1933.

<sup>&</sup>lt;sup>3</sup> Accepted by  $\tilde{J}$ . Physic. Chem.

<sup>&</sup>lt;sup>5</sup> Ibid., **32**, 441, 1928.

<sup>&</sup>lt;sup>2</sup> Ibid., 570, 1933.

<sup>&</sup>lt;sup>4</sup> J. Physic. Chem., **36**, 2272, 1932. <sup>6</sup> Proc. Roy. Soc., **130A**, 197, 1930.

should remain in the vapour phase. These results are expressed in Table I.

A few points of interest may be noted here concerning the mode of measurement of the pressure, a cathetometer reading to 0.01 mm. being

TABLE I.

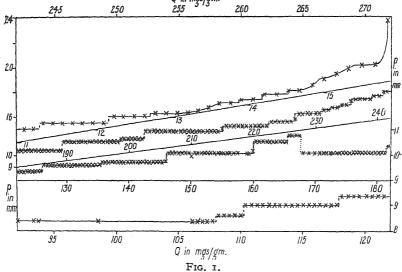
Pre	Quantity of H <sub>2</sub> O adsorbed		
H <sub>2</sub> O.	02	CO 2	in mgs/gm.
1·31 19·31 18·07 16·98 14·18 15·55 16·67 17·90 18·75 19·36 15·74 16·04 23·76	1·31 1·14 2·87 0·61 1·02 0·22 0·35 0·58 0·31	0·50 1·57 1·08 2·57 2·19 1·40 0·66 0·50 0·13 3·92 1·53	60·6 72·6 87·9 106·2 132·0 154·1 173·2 188·9 202·4 214·2 235·8 242·1 271·8

employed. The manometer was of the U-tube type, and the internal diameter of the tubes 2.5 cms. The top of the mercury meniscus was read, the latter being illuminated from behind by diffused light through the glass sides of the thermostat.

After the saturation point had been obtained the desorption isothermal was commenced, the exact course being noted down to 8 mm., and a few more points being taken at intervals down to zero pressure to show the general form of the isothermal in this region. These results are expressed in Fig. 1. The first desorption point gave rise to 0.06 mm.

O<sub>2</sub> and O·31 mm. CO<sub>2</sub>, no further measurable CO<sub>2</sub> being evolved during the experiment, except in the following cases:—

0.05 mm. CO<sub>2</sub> at 236.4 mgs./gm. and 0.20 ,, ,, 167.35 ,, ,, Q in mgs/gm. 245 250 255 260



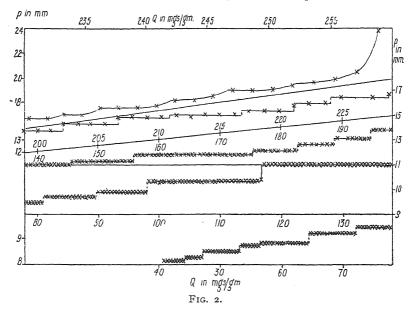
A point of distinct interest was noted in the latter case. Here the pressure rose from 10·1 mm. to 10·78 mm.,  $0\cdot2$  mm.  $CO_2$  being evolved.

This tends to show that a cleaning-up of the surface took place at that point, and that with the removal of  $C_XO_Y$ , some water was now unable to condense in the pores. This is the opposite of what has been found with vapours such as  $CCl_4$ , where a removal of  $CO_2$  causes the pressure to fall.

Twice during the isothermal the quantity calculated by the pressurechange method was checked against a weight determination, the agreement being fairly good in both cases.

Weighed.	Calculated.
167·9 mgs./gm.	170·74 mgs./gm.
105.8 ,,	10б•01 ,,

A few points from this isothermal have been plotted in Fig. 3, to give the general outline and thus make possible a comparison with other



isothermals. A few notes have been made regarding any drift and the rate of attainment of equilibrium. No change in pressure was noted in the following cases over the time interval mentioned.

Quantity adsorbed.	Time interval.
264·68 mgs./gm.	20 hours.
253.94 ,,	20 ,,
118.18 ,,	144 ,,

The equilibrium was slow for the first points on the isothermal, becoming more rapid as the pressure was lowered. This has been shown  $^7$  to be due to a removal of the  $C_{\rm X}O_{\rm Y}$  on the charcoal surface. Below a pressure of approximately 15 mm. there was no change after five minutes.

A resorption experiment was then carried out up to saturation,

<sup>7</sup> Accepted by J. Physic. Chem.

the results being shown in Fig. 3. For the points up to 5 mm., equilibrium was rapid, but at higher pressures it was slower, although no CO2 was detected. The charcoal was then flushed out at 50° and 100° in the usual manner, and heated in contact with liquid water at 100° C.

TABLE II.

Quantity in mgs./gm.

4	
Weighed.	Calculated.
239·I 224·8 212·2 196·8 191·6 174·I 159·3 146·8 112·9 89·9 72·3 56·7	239·22 224·80 212·60 196·64 190·75 175·00 159·74 147·35 112·90 90·00 72·73 57·26

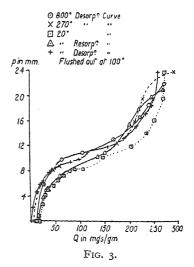
for 3 hours, 29 mm. CO2 being evolved in the process. Undoubtedly this does not represent the total CO, as a certain amount must have dissolved in the water. The charcoal was next desorbed until all excess water had been removed, the quantity figure at saturation—258.9 mgs./gm. —being less than that found previously.

A second desorption isothermal was carried out, the exact course of the isothermal again being determined down to 8 mm. and a few more isolated points obtained to give the general outline of the curve at lower pressures. These results are expressed in Fig. 2. Equilibrium was more rapid than in the previous case, and the rate increased somewhat as the pressure fell. measurable CO, was noted except at a quantity of 211-41 mgs./gm. when 0·1 mm. was found. This is of interest since the pressure at this point rose to the value of the previous step on the evolution of CO2.

The check weights (Table II) were determined during the course of the experiment:-

From this table it will be seen that good agreement has been obtained between the weighed and calculated quantity values. A few points

from this isothermal have also been plotted in Fig. 3, to which have been added isothermals after evacuation at 270° and 800°. In this diagram it is seen that the first desorption isothermal turns over at a low pressure. The resorption curve shows practically no hysteresis at low pressures but a considerable amount is shown at the higher pressures. After flushing out, the quantity adsorbed at saturation was less and the resultant desorption isothermal turned over at a higher pressure than previously, coinciding below 14 mm. with that determined after evacuation at 270°. The 800° isothermal turned over at a still higher pressure. This bears out in general the hypothesis put forward in Part IV. of this series.<sup>2</sup> It is realised that an isothermal carried out on a char-

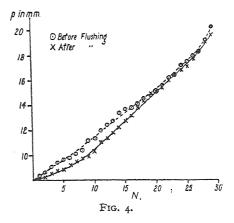


coal which has been evacuated and flushed out at 100° cannot coincide with one evacuated at 800°, since in the former case the  $C_XO_Y$  gives rise to CO<sub>2</sub> and in the latter case to CO almost entirely. In this case, therefore, twice the number of carbon atoms are removed, giving rise to a more open structure which causes the isothermal to sweep over at a higher pressure. This will be dealt with again in the next section of this paper.

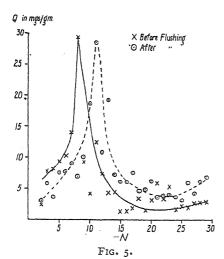
In Fig. 4 are plotted the pressures at which the breaks occur against the sequence of the breaks. Undoubtedly after flushing out the points tend to fall on a smoother curve. The higher and lower pressures do

not alter to any very great extent, but the breaks corresponding to the hysteresis region show a marked drop in pressure values. This points to the removal of some poisoning effect, but it is interesting to note that the actual number of the breaks remains the same.

The actual number of breaks found in this experiment is greatly in excess of that found by the modified retentivity technique. It is known that the presence of  $C_XO_Y$  can cause extra breaks to appear, and since it has



been demonstrated in the next section that there is still some  $C_{\mathbf{X}}O_{\mathbf{Y}}$  on the charcoal surface in this case, it follows that the increased number of breaks may be due to this cause. It is of interest to note that over the pressure range 8-20 mm. in the  $CO_2$  isothermal there are 22 breaks, and in a water isothermal carried out by the modified reten-



tivity technique 6 breaks, the total agreeing with the 29 found in the present experiment

In Fig. 5 are plotted the quantity increments per break against the sequence of the breaks, the continuous curve connecting the points obtained before flushing out and the dotted curve those after. These two curves are seen to be similar with the exception that there is a very slight tendency for the second curve to turn up somewhat at saturation. After flushing out, the individual points lie much closer to the curve than in the previous case, showing that a disturbing effect has been removed. From

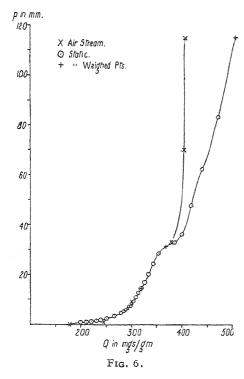
a consideration of this figure it would appear that flushing out causes the values of the quantity increments per break to become smaller at low pressures and greater at high pressures. Again from this diagram it is clear that the isothermal sweeps over at a higher pressure than before, since it has been shown that the number of breaks remain unaltered after flushing out.

In the course of this investigation some 650 experimental points were determined.

A further experiment was carried out on the same sample of charcoal with CCl<sub>4</sub> at 25°. This was undertaken for the following reasons:—

- (I) To find if all the  $C_XO_Y$  had been displaced by the water.
- (2) To determine how the CCl<sub>4</sub> pressure changed with removal of CO<sub>2</sub>, if some C<sub>X</sub>O<sub>Y</sub> were still present.
- (3) To compare the general course of the isothermal with that obtained by withdrawal at constant pressure in an air stream.
- (4) To examine the structure of the isothermal in detail at low pressure and identify the values at which the breaks occur.

The charcoal was charged to saturation at 90 mm. with  $CCl_4$  at room temperature, I mm. of  $CO_2$  being liberated in the cold. The charged charcoal was then heated to 100° for  $4\frac{3}{4}$  hours, 5 mm.  $CO_2$  being evolved and the  $CCl_4$  pressure dropping to 42 mm. It was then left at 100° for  $4\frac{1}{2}$  hours, 2·5 mm.  $CO_2$  being evolved and the pressure dropping to 40 mm. Finally it was again heated to 100° for 4 hours, no  $CO_2$  being evolved, and the pressure remaining the same. Thus 8·5 mm.  $CO_2$  have been removed. Under similar conditions charcoal  $DI^8$  was found to evolve a total amount of 42 mm.  $CO_2$ , thus the water must have removed the



greater part of the  $C_{\mathbf{X}}O_{\mathbf{Y}}$ , for the amounts of  $C_{\mathbf{X}}O_{\mathbf{Y}}$  on these two charcoals are of the same order.

The charcoal was finally charged to 115 mm. at 25° and a desorption experiment carried out, some 183 points being determined. The results are expressed in Figs. 6 and 7, excellent agreement being obtained between the weighed and calculated quantity figures.

#### Discussion.

From Fig. 6 it will be seen that the agreement between the air stream  $^9$  and the static data is good up to 33 mm. At higher pressures, however, the curves diverge, the evacuated charcoal adsorbing 100 mgs./gm. more at saturation. It is probable that this is due to a cleaning up of the last traces of  $C_XO_Y$  from the activation pore by means of

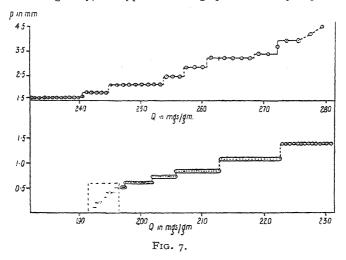
the flushing out technique, whereas in the air stream the  $C_XO_Y$  is only removed from a definite area surrounding each active centre. Again

<sup>8</sup> Proc. Roy. Soc., 130A, 610, 1931.

<sup>9</sup> Trans. Faraday Soc., 29, 564, 1933.

the actual shape of the isothermal is interesting in view of its similarity to the isothermals obtained using silica gel, 10 thus giving rise to a rudimentary type of water isothermal. This will not be discussed here, however, as it has formed the subject of further investigation.

Fig. 7 shows that the isothermal at low pressures is composed of a series of well-marked steps. The dotted area consists of a number of pressure readings only, the apparatus being opened to the pumps between



each determination. The quantity values are unknown, but the object was to obtain the pressures at which the steps occur. The quantity values at 0·I mm. which have been obtained by different methods are given in Table III.

From these figures it would appear that the air stream method gives the same result as  $800^{\circ}$  evacuation, whereas, the best result is obtained by flushing at 100°. It has been shown that comparatively little  $C_{\mathbf{X}}O_{\mathbf{Y}}$ 

is removed by evacuation at 110°, whereas much more is removed by charging in an air stream. Evacuation at 800° will undoubtedly clean up a large number of pores, thus giving rise to an increased adsorptive area. At the same time, however, evacuation at 800° causes the  $C_XO_Y$  to split up almost entirely into CO, whereas if flushing out at 100° be employed, the  $C_XO_Y$ 

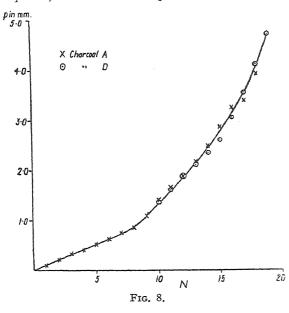
TABLE III.

Method.	Quantity at o'r mm.
110° evacuation 11 800° ,, 6 New Air Stream 2 Static 100° Flushing out 100°	112 mgs./gm. 174 ,, 177.7 ,, 199.7 ,,

is removed as  $\mathrm{CO}_2$ . Hence a great number of carbon atoms, which are removed in the former case, remain in the latter, and these constitute additional active centres. Thus one would expect it to adsorb more at low pressures and this is borne out in practice. Further support for this is given by a comparison of the  $\mathrm{CCl}_4$  isothermals determined on two samples of charcoal, one of which was evacuated at IIO° and the

other at 800° for 80 hours, flushing out at 100° being finally employed in each case.7 The charcoal evacuated at 110° was found to adsorb more vapour than that evacuated at 800°, which is in agreement with the results of the present investigation.

In Fig. 8 the pressures of the breaks have been plotted against their sequence, the data for CCl4 on Charcoal D1 being superimposed. It



will be seen that the points lie on a smooth curve within experimental error, those for Charcoal DI being the more accurate at higher pressures. Since these two charcoals have different starting materials and activated different methods, would appear that the pressures the breaks at lower pressures are independent of these factors. both these charcoals are underactivated. however, it does not follow that breaks are inde-

pendent of the degree of activation. Work in this connection is now being carried out.

#### Summary.

I. The effect of  $C_X^{\infty}O_Y$  on the sorption of water vapour by charcoal has been investigated, some 650 experimental points being obtained.

2. The water isothermal, obtained after flushing out, has been com-

pared with those obtained after evacuation at higher temperatures.

3. The detailed form of the isothermal has been obtained between 23.76 mm. and 8 mm. and the pressure and quantity increments of the steps noted and discussed.

4. A CCl<sub>4</sub> isothermal has been determined on the same sample of charcoal and a comparison made with one obtained by desorbing to con-

stant pressure in an air stream.

5. The detailed structure of the isothermal has been obtained below 4 mm. and a comparison has been made between the pressures at which the steps occur and those obtained with CCl4 on another charcoal.

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# STUDIES ON ADSORPTION.—PART VI.—A COM-PARISON OF THE ISOTHERMALS OF CARBON TETRACHLORIDE AND CARBON DISULPHIDE ON CHARCOAL.

By L. J. BURRAGE.

Received 20th April, 1933.

Measurements on the sorption of carbon disulphide by a series of charcoals, at low pressures under vacuum conditions, resulted in the charcoals being placed in the same order of merit as when using carbon tetrachloride, with one exception—Charcoal A³—which had relatively a much greater capacity for carbon disulphide than for carbon tetrachloride. As, at low pressures, the simple retentivity test, using carbon tetrachloride, agave results closely corresponding with those obtained by the static technique, it was decided to carry out similar tests with carbon disulphide in order to see whether this anomaly would remain, and whether the same general concordance between the results of such tests and those of the static experiments still existed.

The experimental details were the same as in the case of carbon tetrachloride, except in the matter of the initial charging pressure. It seemed preferable that in charging the charcoal columns, the same relative and not the same absolute pressures should be used to obtain comparable results. This involved the use of a carbon disulphide pressure about three times that of the corresponding carbon tetrachloride, i.e., 100 mm. as against 33 mm.

The following charcoals were employed in this investigation:—

Table I. contains, for the above charcoals, the saturation quantity values in mgs./gm. (1) at the charging pressure of 100 mm. at 100° C and (2) during the desorption process at f(p) = 1, i.e., at conditions equivalent to  $2 \times 10^{-2}$  mm. at 25°. Column (3) shows the data obtained by the vacuum technique at  $2 \times 10^{-2}$  mm. at 25°. All the results are expressed as mgs./gm.

The agreement between data in columns (2) and (3) is seen to be fairly good, the charcoals standing in the same order, and, in particular, the unexpected position of A being confirmed. Table II. contains the corresponding retentivity test data obtained with carbon tetrachloride.

Proc. Roy. Soc., 134A, 555, 1932.
 J. Physic. Chem., 32, 441, 1928.
 Ibid., 129A, 235, 1930.
 Jour. Soc. Chem. Ind., 47, 372, 1928.

Columns (I) and (2) have similar significance to the corresponding columns in Table I.

A comparison of the two sets of low pressure figures shows that, under the retentivity test conditions, A and DI give relatively better

TABLE I.

TABLE II.

Charcoal.	(1)	(2)	(3)	Charcoal.	(1)	(2)
B K E F C H L A D <sub>I</sub>	122·7 167·4 126·5 195·5 228·8 211·1 240·2 179·9	9 12 14 30 32 35 36 38 45	10 16 	B E K A D1 F H C L	352·6 247·1 408·6 172·7 210·6 300·1 323·4 275·5 424·5	47 65 72 84 95 113 116 125

results with carbon disulphide than with carbon tetrachloride. At the initial charging pressure the change from carbon disulphide to carbon tetrachloride in all cases leads to an increase in the weight of sorbate taken up, the multiplying factor varying from about I·I (DI) to 2·9 (B) except in the case of A, where there is actually a decrease.

#### Discussion.

In a previous publication <sup>1</sup> it has been stated that carbon disulphide might be a far more powerful agent for the displacement of tenaciously adsorbed oxygen than is carbon tetrachloride, owing to the absence of drift in all isothermals. If this is the case it is difficult to see why there should be more CO<sub>2</sub> evolved during the course of an experiment than with CCl<sub>4</sub>. In the present paper it is suggested that the reverse may be the case, *i.e.*, that CS<sub>2</sub> is only a comparatively feeble agent in the removal of CO<sub>2</sub>. In the case of adsorption by unactivated charcoal <sup>5</sup> it was found that in some instances a large proportion of the adsorbed substance was held as a quasi-chemical compound at zero pressure, the amount thus held being dependent on a particular atom and its position in the molecule. This could hardly be ascribed to a cleaning-up effect, since the charcoal would be activated in the process, and this was not found to be so in the case of CS<sub>2</sub>.<sup>5</sup>

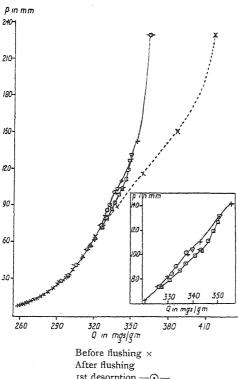
It has also been found, when using substances of this type, that by charging at a constant pressure the quantity of substance adsorbed—time curve passes through a maximum. This would be the case if the air stream were sweeping away some of the  $C_XO_Y$  to which the  $CS_2$ , for example, is attached.  $CO_2$  has been shown to be present in the effluent gas, hence the above picture of the mechanism would appear to be sound. In view of this, the results in the previous paper 1 must be re-examined and the alternative possibility put forward. It has been stated that one unexpected feature was the liberation of amounts of  $CO_2$ , when working with  $CS_2$  which were far higher than those normally observed with  $CCl_4$ . This latter, however, has been found by the author to break up the  $C_XO_Y$  more readily than does  $CS_2$ .

<sup>&</sup>lt;sup>5</sup> Trans. Faraday Soc., 29, 458, 1933.

This may occur because CCl<sub>4</sub> cannot attach itself to the surface complex but must clean up the surface before adsorption can take place.

Thus,  $CS_2$  being the more feeble cleaning agent, causes a slow evolution of  $CO_2$  throughout the experiment. This cannot be accompanied by drift, however, for  $CS_2$  is being lost by the charcoal, since some  $C_XO_Y$  to which the  $CS_2$  was attached has been removed. The degree to which this effect will take place will depend on the ease with which the  $CO_2$  is liberated. This hypothesis gives an explanation of why the resorption curves lie to the left of the original curve in Fig. 4 in a previous publication.<sup>1</sup>

A further point in support of the hypothesis that  $CS_2$  does not clean up the surface readily is shown by a comparison of the amounts of  $CS_2$  and  $CCl_4$  held at 1 in f(p). Since the



Before flushing ×
After flushing
1st desorption —⊙—
1st resorption ↑
2nd desorption ♂
3rd desorption ⊡
3rd resorption ⊙
Fig. 1.

Mol. Wt. of CS<sub>2</sub> is half that of CCI<sub>4</sub> the quantities of the latter have been halved and the results should be similar for the two substances. The quantities are expressed in mgs./gm.

Now, if CS<sub>2</sub> is the better agent for cleaning up, the quantities of CS<sub>2</sub> should be greater than for On the contrary CCl<sub>4</sub>. they are smaller in every case, especially so with charcoals which have little  $C_{\mathbf{X}}O_{\mathbf{Y}}$  on the surface. This points strongly to the fact that the  $C_XO_Y$ is only very slowly removed by the CS<sub>2</sub> and that the latter is actually being taken up by the complex.

This may be due in part to CS<sub>2</sub> behaving in a similar fashion to CO<sub>2</sub> and not like the vapours which cannot be adsorbed in a quasi-chemical form. In this case the CS<sub>2</sub> order will be the same as the capacity of the charcoals for CO<sub>2</sub>. A large number of charcoals have been examined by Allmand

and Chaplin, but one cannot obtain the order of the individual charcoals

<sup>&</sup>lt;sup>6</sup> Proc. Roy. Soc., 132A, 460, 1931.

as regards their capacity for CO<sub>2</sub> as this was found to vary greatly with the degree of evacuation and other methods of treatment. All one can say is that chemically activated charcoals are much poorer in this respect than the others, and this has also been found to be the case

with  $CS_2$ .

To test some of the views put forward in this paper, an isothermal was carried out with  $CS_2$  at 25°, employing the vacuum technique, on Charcoal A, which had been found to possess considerable quantities of tenaciously held oxygen. The charcoal was then flushed out at 100° and the isothermal redetermined. It was found that  $CS_2$  did not break up the  $C_XO_X$  as readily as did  $CCl_4$ , but the total amount of combined oxygen liberated after several flushings out was 43.5 mm., which was similar to the amount obtained with  $CCl_4$  on Charcoal D1.

The results are shown in Fig. 1, where it will be seen that, before flushing out, the isothermal gives a fairly large sweep over which is almost entirely lost after the  $C_X O_Y$  has been removed. The inset on Fig. 1 shows that this isothermal possesses a very definite hysteresis loop which is reversible. Hence the isothermal shows that it has all the rudimentary characteristics of the water type. This is a point of distinct importance as it demonstrates that in all probability all isothermals are of this general type, and it is merely a question of degree as to whether an isothermal conforms to the so-called "water-type" or "normal vapour type."

A similar sweep over has already been shown to occur with a  $CCl_1$  isothermal on the same charcoal. This will not be discussed here as it has formed the subject of a further investigation. The fact that the charcoal takes up less at higher pressures after flushing out is in accordance with the views expresseed in Part V. of this series, since water and  $CS_2$  can both be adsorbed by the  $C_XO_Y$ .

#### Summary.

Tests have been carried out on the relative capacity of charcoals for CCl<sub>4</sub> and CS<sub>2</sub> at high and low pressures.

Certain anomalies in the relative order of the charcoals have been discussed and a hypothesis advanced as to the mechanism in these cases.

An isothermal has been determined for  $CS_2$ , which gives rise to a reversible hysteresis loop. The  $CO_2$  liberated from the  $C_XO_Y$  on the surface has been noted.

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<sup>7</sup> Part V., page 668.

# A FURTHER CRITICISM OF ACTIVATED ADSORPTION.

By L. J. Burrage.

Received 25th April, 1933.

For many years the difficulty of removing the last traces of oxygen from a charcoal surface has been recognised, Langmuir stating that oxygen was completely removed from graphite only after heating to 2000° C. for half an hour in the highest vacuum, while Lowry and Hulet also agree that oxygen is not completely removable at 1180° C. The effect of this combined oxygen on adsorption isothermals has been emphasised by the author in a number of papers, and in particular the specific effect on activated adsorption has been discussed, the views expressed in the latter paper being in agreement with those of Keyes and Marshall. Taylor and Williamson calculate the energy of activation from the following formula:—

$$\log \frac{t_2}{t_1} = \frac{Q}{R} \left( \frac{\mathbf{I}}{T_2} - \frac{\mathbf{I}}{T_1} \right),$$

where  $t_1$  and  $t_2$  are the respective times at temperature  $T_1$  and  $T_2$ , which are necessary for the same volume to be adsorbed. Thus the energy of activation depends entirely on the ratio of the times in which a certain quantity is adsorbed at two different temperatures. It has been shown by the author <sup>6</sup> that the evolution of  $CO_2$  from the charcoal surface during sorption caused a big jump in the speed, hence the cleaner the surface the faster will be the rate of adsorption. This has been noted by other authors, for Sameshima <sup>7</sup> states that rigorous evacuation enormously reduces the time required for equilibrium to be attained, while both Harned <sup>8</sup> and Sheldon <sup>9</sup> illustrate this by the changes in the velocity laws during the course of the sorption of a gas by charcoal.

Taylor states that a certain portion of the adsorption takes place at once and this is followed by a slower process which he terms activated adsorption. The author has shown that, by adopting the flushing-out technique, 10 adsorption is instantaneous or almost so over the whole pressure range for fairly large quantity increments, hence there can be little or no activated adsorption in this case, but this experiment was carried out on a charcoal which had been found to exhibit drifting properties to a marked degree. 11 Thus in the latter case there is activated adsorption while in the former it is practically absent, although the temperature, charcoal and vapour are the same in both cases.

In some recent work <sup>12</sup> it has been found that with CCl<sub>4</sub> isothermals drift was only noticeable with underactivated charcoals. Hence it

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    J.A.C.S., 38, 2276, 1916.
    Trans. Faraday Soc., 28, 194, 1932.
    Ibid., 53, 2168, 1931.
    Bull. Chem. Soc. Japan, 2, 1, 1927.
    Phys. Res., (2) 16, 165, 1920; 19, 253, 1922.
    Accepted by J. Physic. Chem.
    Trans. Faraday Soc., 29, 564, 1933.
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follows that more vapour molecules are held by activated adsorption in the case of an underactivated charcoal than in that of a more highly activated charcoal, which does not seem a reasonable hypothesis. On the other hand the author has already put forward views as to why the  $C_{\mathbf{X}}O_{\mathbf{Y}}$  is more difficult to remove from underactivated charcoals, thus giving rise to the observed drift.  $^{13}$ 

It is unnecessary to assume that certain molecules acquire an activation energy of adsorption in this process, for the cleaning up effect in the flushing-out technique would appear to be the result of the following mechanism. To remove all the  $C_XO_Y$  it is necessary to have a large quantity of vapour sorbed on the surface and also carry out the process at a fairly high temperature. Since  $C_XO_Y$  gives rise to a vapour pressure of  $CO_2$  at room temperature, by employing a temperature of  $IOO^\circ$ , the tendency for  $C_XO_Y$  to vaporise as  $CO_2$  is increased, and the presence of a large number of vapour molecules in both the adsorbed and gaseous phases prevents the return of the  $CO_2$  to the charcoal surface. Hence the  $C_XO_Y$  is removed as  $CO_2$ , the latter molecules being replaced by vapour molecules. Although these remarks apply primarily to a charcoal surface, the same difficulty is met with in removing oxygen from metal surfaces.

It has been found that the cleaning up of the surface gives rise to a larger number of vapour molecules retained at zero pressure, or more chemisorption, if the vapour cannot be adsorbed by the  $C_XO_Y$ , and less adsorbed if the molecules are retained by the complex.<sup>14</sup>

Some recent work by McKinney  $^{15}$  on the adsorption of hydrogen by MnO .  $\rm Cr_2O_3$  has a distinct bearing on the point in question. He states that the surface reaches a maximum activity and remains quite constant. This does not mean that all traces of foreign gases have been removed from the metal surface since reversible isothermals have been obtained on charcoal which had a considerable amount of  $\rm C_XO_Y$  present. When this was removed, however, the quantity value at any given pressure was increased, as well as the rate of attainment of equilibrium. He also finds that his first adsorption figures agree with those of Taylor and Williamson, but successive treatments increase the amount adsorbed in a given time. Since Taylor calculated the energy of activation from experiments, which, in each case, consisted of one sorption experiment, and did not carry out any further resorption, it shows that the calculated figures have probably but little meaning.

#### Summary.

A further criticism of the experimental evidence for an activated energy of adsorption has been advanced and a number of cases quoted which arise from recent investigations.

King's College, London.

<sup>13</sup> Trans. Faraday Soc., **29**, 445, 1933. 
<sup>14</sup> Unpublished work. 
<sup>15</sup> J. Physic. Chem., **37**, 381, 1933.

# THERMODYNAMICAL STUDY OF SYSTEMS OF THE TYPE PbCl, - RCl - H,O AT 25° C. PART II.

By A. J. Allmand and L. J. Burrage.

Received 13th April, 1933.

In Part I.1 of this series, the electrometric technique employed was described, and a general account given of the results obtained with the system PbCl<sub>2</sub>-KCl-H<sub>2</sub>O, and of their working up. The present paper contains a record of the final results, and of their definitive treatment. Some further measurements have been made since the first publication. and the results as a whole are now reconsidered in the light of the revised equilibrium data recently published.2

### Experimental Data.

Table I. comprises the results obtained at 25° when working with thecell

Pb (amalgamated) 
$$\mid$$
 PbCl<sub>2</sub> + KCl  $\mid$  Ag AgCl (solid)

and using unsaturated solutions. Measurements made on cells in which [KCl] 3 was zero are not included. The two figures given for each concentration pair are respectively the average value (of three to eight separate results) for the E.M.F. in volts, and the activity 4 of the dissolved PbCl<sub>2</sub>, calculated from the equation  $\log a_1 = (0.4837 - E)/0.02957$ , where 0.4837 volt represents the E.M.F. of the above cell when PbCl, is present as a solid phase. The root-mean-square errors of the values for E were of the order of  $2 \times 10^{-4}$  volt.

Measurements were also made with one or more of the possible solid phases (viz., PbCl<sub>2</sub>; 2 PbCl<sub>2</sub>, KCl; PbCl<sub>2</sub>, KCl, I/3 H<sub>2</sub>O; KCl) present. When KCl was the solid phase, [PbCl<sub>2</sub>] was directly determined, and [KCl] subsequently read off from the equilibrium diagram. (In doing this, the solubility of KCl in absence of PbCl2 has been taken as 4.81 M. or 359 grams/1000 grams H2O, which is the usually accepted figure, and which differs slightly from the value 5 of 361 grams/1000 grams H<sub>2</sub>O, hitherto used by us.) In other cases, [PbCl<sub>2</sub>] was usually not determined experimentally, but read off from the equilibrium diagram.

Over the greater part of the concentration range, no difficulty was experienced; the observed values of E.M.F. were reproducible, or else fell on to the smooth curve drawn through the various points within

<sup>&</sup>lt;sup>2</sup> Ibid., 28, 529, 1932. <sup>1</sup> Trans. Faraday Soc., 23, 470, 1927. <sup>3</sup> All concentrations are referred to 1000 grams of water.

<sup>&</sup>lt;sup>4</sup> In these papers, the activities of the various components of the system (a<sub>1</sub>, PbCl<sub>2</sub>; a<sub>2</sub>, RCl; a<sub>3</sub>, H<sub>2</sub>O) are all expressed as fractions of the activities of the pure components.

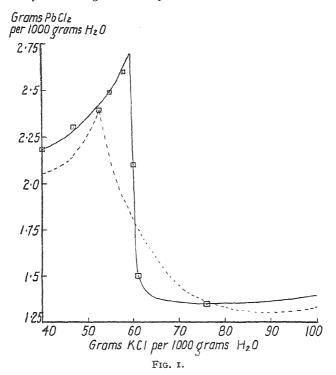
Trans. Chem. Soc., 1703, 1926.

	330	1	1		1		1	.5188	.5155 .0841
-	292	0.5661	.5523 .00479	.5392	.5272	·5213	.5184	.5132 .1006	
	231	0.5543	.5415 .0111	.5293 .0286	2690.	.5123	·5086 ·1438		1
	170	0.5456	.5315	.5209	·5092 ·1373	·5033 ·2173	1	1	1
	130	0.5397	.5263 .0362	.5147 .0895	·5030 ·2224	ı	1	1	
	96	0.5339 .0201	.5211 .0543	·5094 ·1352	.4975 .3414	ı	I	ı	
<u></u> 된	89	02495	.5188 .0650	.5071 .1616	.4946 .4280	1	l	1	l
TABLE	52	0.5296	.5172 .0736	·5056 ·1818	.4937 .4588	.4885 .6880	.4860 .8360	1	1
	35	0.5311 .02495	.5176	.5057 .1803	·4939 ·4520	.4880 .7155	.4849 .9107	l	
	15	6910.	.5238	.5123	.5003	.4939	.5751	l	
	7.5	0.5422	·5290 ·0294	.5184 .0671	.5070 .1629	.5012 .2560	.4975 .3416	.4909 .5709	
	3.75	0.5480	.5362 .01675	·5256 ·0383	.5149 .0881	·5090 ·1394	.5046 .1964	.4978 .3336	.4884
	Grams Grams PbCl <sub>2</sub> .	0.125	0.25	0.5	0.1	1.5	2.0	3.0	4.0

the experimental error. But between the concentrations of 55-75 grams KCl/1000 grams  $H_2O$  (0·75—1 M.), the state of affairs was different. Just as, in this concentration region, subsequent work has shown the aqueous vapour pressures of the solutions to show remarkable anomalies, so it proved impossible to obtain really satisfactory E.M.F. values for solutions either saturated or in the neighbourhood of saturation. Although giving consistent readings themselves at the time, such solutions tended to behave as if they were either supersaturated or unsaturated. Thus, in the earlier stages of the work, the value of 0·4899 volt was found for a cell filled with a solution containing 68 grams KCl and 1·5 grams PbCl<sub>2</sub> per 1000 grams  $H_2O$ , and with solid 2 PbCl<sub>2</sub>, KCl present. Later work has shown such a solution to be supersaturated, and the figure

just quoted is consistent with this view. On the other hand, early measurements gave E=0.4867 volt for a solution of composition (in grams) PbCl<sub>2</sub> 2; KCl 57; H<sub>2</sub>O 1000, and supposed to be saturated with the same double salt. Later measurements ascribed the same E.M.F. to a solution of composition PbCl<sub>2</sub> 2.28; KCl 58.5; H<sub>2</sub>O 1000, again imagined to be in equilibrium with the double salt. Our present interpretation attaches this E.M.F. to a solution with PbCl<sub>2</sub> 1.9; KCl 60.35; H<sub>2</sub>O 1000; the two former solutions are now regarded as unsaturated.

The uncertainty referred to is closely connected with the difficulty of defining the equilibrium diagram in this region. This is perhaps best indicated by remarking that the position of the triple point PbCl<sub>2</sub>;



2 PbCl<sub>2</sub>, KCl; solution has, at successive stages in the work, been placed at

52·5 grams KCl: 2·39 grams PbCl<sub>2</sub>
55 ,, ,, : 2·49 ,, ,,
58 ,, ,, : 2·67 ,, ,,
59 ,, ,, : 2·7 ,, ,,

Both solid phases were actually present during the first two measurements, and solid PbCl<sub>2</sub> during the third. But the fourth is merely an extrapolation, and indeed the triple point has not been satisfactorily determined experimentally. Fig. 1 shows the configuration of the equilibrium diagram in this region both as finally adopted and as at first assumed (dotted curve).

Table II. contains the data for those E.M.F. values given by saturated

[KCl] in gra 1000 gra	[PbCl <sub>2</sub> ] ams per ams H <sub>2</sub> O.	Solid Phase	E in volts.	$a_1$ .
0 7*5 35 55	10·94 4·70 2·22 2·49	PbCl <sub>2</sub>	0·4836 ·4837 ·4837 ·4837	1.0 1.0 1.0

Region of unreliable readings.

				ł
75 90 130	1·35 1·37 1·49	2 PbCl <sub>2</sub> , KCl.	·4923 ·4942 ·4981	0·5106 0·4415 0·3258
170	1.88	2 2 2012, 2201.	.2011	0.2580
182	2.04		•5020	0.2404
231	2.91	2PbCl <sub>2</sub> , KCl+ PbCl <sub>2</sub> , KCl, 1/3 H <sub>2</sub> O	.5050	0.1904
238	2.98	2 7 2	·5058	0.1788
265	3.41		·5085	0.1449
292	3.91	PbCl <sub>2</sub> , KCl, 1/3 H <sub>2</sub> O	.5107	0.1221
299	4.04		.5117	0.1129
330	4.65		.5141	0.0938
361	5.25	PbCl <sub>2</sub> , KCl, $1/3$ H <sub>2</sub> O $+$ KCl	.5164	0.0783
362.5	4 \	•	.5198	0.0601
362	3		.5234	0.0454
361	2		.5284	0.0308
360.5	1.5	KCl	.5333	0.0210
360	r		.5403	0.0122
359.5	0.5		.5540	0.0042
359	0.25		.5701	0.0012
359	0.125		•5893	0.0002
-				

solutions which are not subject to serious question.

The E.M.F. figures finally attributed to cells made up with solutions saturated with 2 PbCl<sub>2</sub>, KCl in the concentration region 59-75 grams KCl/1000 grams H<sub>2</sub>O were obtained as follows. The experimental figures for unsaturated solutions and for saturated solutions as far as these were reliable were plotted on a large scale in the form of E against  $\log$ [PbCl<sub>2</sub>], a separate graph of course resulting for each value of [KCl]. The points corresponding to the data in Table II. for KCI concentrations of 75-231 grams/1000 grams

water inclusive were joined by a tie-line, characterised by the presence of 2 PbCl<sub>2</sub>, KCl as a solid phase. It was assumed, in accordance with

TABLE III.—Saturated Solutions in Equilibrium with 2 PbCl $_2$ , KCl. Concentrations in Grams per 1000 Grams of  $\rm H_2O$ .

[KCI].	[PbCl <sub>2</sub> ].	E (volts).
59 59·5 60 60·5 61 62 63 65 68 70	2·7 2·4 2·1 1·8 1·5 1·45 1·39 1·36 1·36	0·4837 ·4846 ·4857 ·4872 ·4891 ·4895 ·4897 ·4902 ·4909 ·4913 ·4922

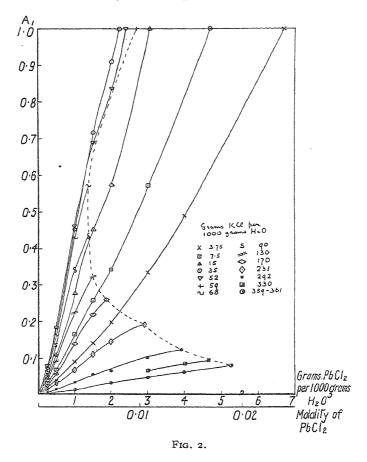
TABLE IV.

E.	$a_1$ .			
0.4844 volt .4851 .4858 .4866 .4875 .4883 .4892 .4903 .4926 .5044 .5133 .5222 .5340	0·95 0·9 0·85 0·8 0·75 0·75 0·65 0·6 0·5 0·2 0·1 0·05 0·02			

# CORRIGENDA.

Page 683: The point  $A_1O$ , Grams PbCl<sub>2</sub> 5.6 should be deleted. Page 686: Reference 12 is: "Unpublished work from this laboratory." In Table V all the figures in  $N_1$ , except those three which are asterisked, should be divided by ten.

Fig. 1, that this saturation curve would start out at 2.7 grams  $PbCl_2/1000$  grams  $H_2O$  and at 0.4837 volt, and the tie-line was continued, on what appeared to be its most probable course, so as to pass through this point. The essential correctness of the resulting curve received some support from the fact that the  $E/\log$  [PbCl<sub>2</sub>] graph for unsaturated solutions containing 68 grams KCl/1000 grams  $H_2O$ , when normally produced, cut the tie-line at a point very close to the PbCl<sub>2</sub> figure of 1.36 grams shown in Fig. 1. A similar procedure was carried through, using diagrams in which E was plotted against [PbCl<sub>2</sub>] (instead of log [PbCl<sub>2</sub>]) for various



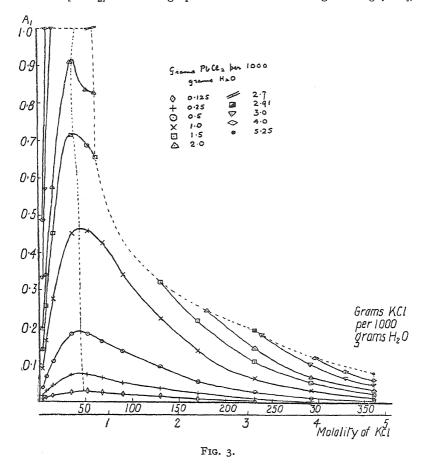
constant concentrations of KCl, and against [KCl] for various constant values of [PbCl<sub>2</sub>].

The final results computed for this region, in which it is hoped that the arbitrary factor has been reduced to a minimum, are contained in Table III. If the values of E be plotted against [PbCl<sub>2</sub>] and against [KCl], the latter curve appears somewhat distorted between the concentration limits of 59-61 grams KCl/1000 grams H<sub>2</sub>O. But it could only be "corrected" by making arbitrary changes in the analytical data, and at present we are basing our treatment of the question on the

assumption that these data are essentially more reliable than E.M.F. measurements in this region. Whether this can be substantiated remains to be seen.

# Treatment of Results.

The measured values of E were plotted, as mentioned above, against  $[PbCl_2]$  and against  $[BbCl_2]$  at constant  $[BbCl_2]$ , and against  $[BbCl_2]$ . Similar graphs were drawn for E against  $[BbCl_2]$ .



and, from the ensemble of curves, the most probable values of simultaneous KCl and PbCl<sub>2</sub> concentrations read off which corresponded to certain definite fractional values of E, these, in turn, corresponding to definite fractional values of  $a_1$ , as calculated from the expression  $\log a_1 = (0.4837 - E)/0.02957$ . Table IV. contains the E and  $a_1$  values employed. In addition, the values of  $a_1$  directly calculated from the experimental data were plotted against [PbCl<sub>2</sub>] and against [KCl], as <sup>6</sup>

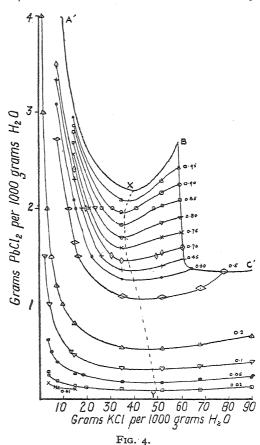
<sup>&</sup>lt;sup>6</sup> The dotted tie-lines in Figs. 2 and 3 correspond to the presence of a solid phase.

in Figs. 2 and 3, and the concentrations corresponding to the above series of round values read off.

# Lead Chloride Isodynes.

The resulting data were plotted on the equilibrium diagram in the form of PbCl<sub>2</sub> isodynes, *i.e.*, curves of constant lead chloride activity.

Fig. 2 of Part I. gives a general idea of the relations found, and we will confine ourselves to reproducing in Fig. 4 the curves in the neighbourhood of the concentration region where the experimental difficulties described above were Along experienced. A'B, PbCl<sub>2</sub> is the solid phase—it therefore represents the isodyne for  $a_1 = I$ . BC' is the solubility curve of 2 PbCl<sub>2</sub>, KCI. The marked points through which the isodynes are drawn have been read off from the curves expressing the experimental data as described above. XY passes through minima of the different curves and indicates, for any value of [PbCl<sub>2</sub>], the optimum amount of KCl which can be added without decreasing  $a_1$ . It should be identical in course with the curve drawn through the peaks of the graphs in Fig. 3.



# Evaluation of $a_2$ and $a_3$ for Saturated Solutions.

The procedure employed has been explained in Part I. We shall, therefore, merely draw attention to any change in the data used, and record our final results.

(i) The value of  $a_3$  for a saturated solution of KCl (point E in Fig. 6) forms the starting point of these calculations. Taking 359 grams/1000 grams  $H_2O$  as the solubility, the following data were available:—

Lovelace, Frazer and Sease, 7 0.8439 (extrapolated from 20° C.).

Pearce and Snow,8 0.8420; 0.8443.

Leopold and Johnston,9 0.8418 (interpolated).

Hepburn.10 0.8435.

Hunter,11 0.8429 (mean value). Weir,12 0.845 (mean value).

We selected the figure 0.844, and graphical integration along ED. using the relation

$$\int d \ln a_3 = -\int \frac{N_1}{N_3} \cdot d \ln a_1,$$

gave  $a_3 = 0.8435$  at D.<sup>13</sup>

(ii) Along CD, i.e., for solutions saturated with PbCl<sub>2</sub>, KCl, 1/3 H<sub>2</sub>O, the relation

$$\log a_1 + \log a_2 + 1/3 \log a_3 = constant$$

holds good, and the data for point D fix the value of the constant at 2.8692. The use of this equation and of graphical integration, employing the expression

$$\int\! d\, \ln\, a_3 = \int\!\! \frac{3(N_2-N_1)}{3N_3-N_2} \, . \, d\, \ln\, a_1,$$

gave the values of  $a_2$  and  $a_3$  at any point on CD. At C, they were 0.4026 and 0.8995 respectively.

TABLE V.

N <sub>1</sub> .	$N_2$ .	$a_1$ .	$a_2$ .	a <sub>3</sub> .
0.01895*	4.840	0.0783	1.0	0.8435
.1668	.424	.0938	0.8310	.8567
·1460	.025	.1139	·68o8	18698
1259	3.620	.1429	.5396	8837
·1086	-218	.1770	*4335	·8958
0.01047 †	•096	1904	•4026	-8995
.0967	2.949	.2010	.3612	.9048
.0773	-548	•2331	•2685	-9181
.0633	•145	.2724	•1966	.9305
.0536	1.743	.3232	•1396	.9417
·0500	·34I	•3989	.0917	•9526
.0485	o·938	•5534	.0477	•9649
·0500	·87I	.6027	.0402	•9679
.0539	-818	.6566	•0339	.9703
·0647	·811	.7614	.0252	.9745
·0755	·8o4	·8559	•0199	.9779
0.00971 ‡	•791	1.0	·0146	-9822

<sup>\*</sup> Point D.

<sup>†</sup> Point C.

<sup>‡</sup> Point B.

<sup>7</sup> Jour. Amer. Chem. Soc., 43, 102, 1921.

<sup>8</sup> Jour. Physical Chem., 31, 231, 1927.

<sup>10</sup> Trans. Chem. Soc., 553, 1932.

<sup>&</sup>lt;sup>9</sup> Jour. Amer. Chem. Soc., 49, 1974, 1927.
<sup>11</sup> Unpublished work from this laboratory.

<sup>&</sup>lt;sup>18</sup> N<sub>1</sub> N<sub>2</sub> N<sub>3</sub> are respectively the molar fractions of PbCl<sub>2</sub>, KCl, and H<sub>2</sub>O.

(iii) Along BC, i.e., for solutions saturated with 2 PbCl<sub>2</sub>, KCl, the relation

$$2 \log a_1 + \log a_2 = constant$$

holds good, and the value of  $\bar{2}\cdot 1641$  follows from the data of point C. Using this relation and graphical integration in accordance with the equation

$$\int\!d\,\ln\,a_3 = \int\!\!\frac{2N_2-N_1}{N_3}\,.\;d\,\ln\,a_1,$$

the values of  $a_2$  and  $a_3$  could be deduced for any point along BC. At B,  $a_2$  and  $a_3$  are 0.0146 and 0.9822 respectively.

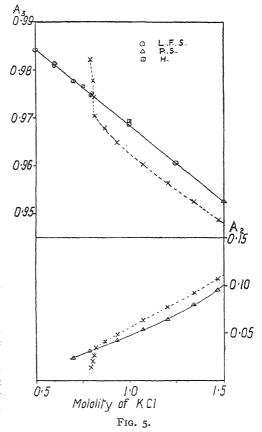
In Table V. are collected the values of  $a_1$ ,  $a_2$ , and  $a_3$  for a few points along the curves BC and CD.  $N_3$  is 55.5 throughout.

# Potassium Chloride and Water Isodynes.

Using a large-scale graph of relative aqueous vapour pressure  $(a_3)$ 

plotted against [KCl],  $^{14}$  the values of  $a_2$  for pure KCl solutions were calculated by graphical integration, and plotted against [KCl]. These two curves for pure KCl solutions were then compared with in which graphs  $a_2$ and  $a_3$  for solutions saturated with the two double salts were plotted against [KCl].

The corresponding graphs lie very close to one another over the greater part of the concentration range corresponding to the existence of the double salt PbCl<sub>2</sub>, KCl, 1/3 H<sub>2</sub>O, but diverge more markedly in the region of existence of 2PbCl<sub>2</sub>, KCl. "solid phase" curves in both cases (as also the corresponding  $a_1$  curve) of course consist of two branches, the invariant point at C being plainly visible. Those for  $a_3$  lie throughout at almost rather lower activity

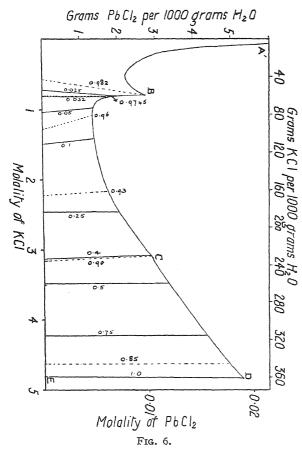


values than the curve for pure KCl, the separation being imperceptible

<sup>14</sup> See Lovelace, Frazer and Sease; Pearce and Snow; Hepburn (loc. cit.).

at high values of [KCl], but considerably greater at  $1-1\cdot 5$  M. In this region, the graph shows an inflection; concave to the origin at higher concentrations, it begins to bend up rapidly in the direction of the  $a_3$  axis, and crosses the curve for pure KCl solutions at 0.81 M.

The "solid phase"  $a_2$  graph is almost coincident with, whilst crossing, the curve for PbCl<sub>2</sub>-free solutions in the 2 PbCl<sub>2</sub>, KCl, 1/3 H<sub>2</sub>O region. It lies above the pure KCl curve at lower concentrations, but very rapidly drops at about 0.83 M., crossing the KCl curve at [KCl] = 0.82 M. Fig. 5 (continuous curves pure KCl; dotted curves PbCl<sub>2</sub> present)



illustrates sudden changes of slope. They are, of course, bound up with one another, with the rapid change in direction of the curve in Fig. I. and with the rapid increase in  $a_1$  as 🛪 [KCl] falls (see Table V.). Further investigations in this laboratory have revealed the existence of anomalous and interesting effects in this concentration region; these will be reported later.

Tables VI. and VII. contain data, derived from the curves just mentioned, which, on the assumption that the KCl and H<sub>2</sub>O isodynes are linear, are plotted in Fig. 6 (KCl isodynes continuous, H<sub>2</sub>O isodynes

dotted, lines). One point only need be mentioned. In Part I. (pp. 475-6), a vertical KCl isodyne ( $a_2$  and  $N_2$  identical at the terminal points) was located at [KCl] = 0.91 M., whereas the corresponding vertical  $H_2O$  isodyne ( $a_3$  and  $N_2$  identical at the terminal points) was found at 0.75 M. These two results were inconsistent and unexplained at the time. The new analytical data on the equilibrium system now available, and utilised in this paper, have led to the clearing up of this discrepancy, in that both isodynes are now found to fall at practically the same value of [KCl], viz., 0.81-0.82 M.

Any further discussion (e.g., of the reciprocal effects of the presence

of KCl and of PbCl<sub>2</sub> on their respective activities) will be postponed until the results of measurements with solutions containing NaCl and LiCl instead of KCl are available.

	VI.—TERMIN OF KCl ISODY		TABLI	E VII.—Ter of H <sub>2</sub> O Is	MINAL POINTS
	Molality of KCl.			Molality of KCl.	
$a_2$ .	Pure KCI.	Saturated Solutions of Double Salt.	$a_3$ .	Pure KCl.	Saturated Solutions of Double Salt.
0.75 0.5 0.4 0.25 0.1 0.05 0.032 0.025	3.13	225 475 3.075 45 1.41 0.96 82	0·982 0·9745 0·96 0·93 0·90 0·85	1·27 2·21 3·14	0·79 81 1·075 2·16 3·08

#### Summary.

(1) The final results of an electrometric study of the system PbCl<sub>2</sub>— KCl—H<sub>2</sub>O at 25° C. are described, and discussed in the light of revised analytical data.

(2) The general nature of the isodynes of the three components of the

system is elucidated.

(3) Unexpected and anomalous activity relations have been found in the same concentration region which presented difficulties when the original analytical work was carried out on the system.

King's College,

#### A PHOTO-ELECTRIC SPECTROPHOTOMETER.

By Albert Gordon Winn.

Received 21st March, 1933.

The application by von Halban <sup>1</sup> of the photo-electric cell to spectrophotometry has shown that the photo-electric method is capable of a high degree of accuracy. The instrument described in the present communication was built in connection with photochemical work, partly to improve on the accuracy of the sector-photographic method for the measurement of the extinction coefficient of a photolyte at the wave-

¹ von Halban and co-workers: a series of papers in the Z. physikal. Chem. from 1920 onwards; in particular, von Halban and Siedentopf, Z. physikal. Chem., 100, 208, 1922; and von Halban and Eisenbrand, Proc. Royal Soc., 116A, 153, 1927. For a critical survey of photo-electric spectrophotometry, see also Gibson, "Discussion on Photo-electric Cells," Phys. and Opt. Soc., 157, 1930.

lengths of the mercury lines, and partly to attain the necessary high precision for the study of photochemical reactions by photometric means in cases to which the more usual analytical methods are difficult to

apply.

The von Halban photometer utilises the well-known compensation principle with two photo-cells illuminated by the same light source. An electrometer is used as a null instrument and the ultimate calibration depends upon a rotating sector of variable aperture. Recent experience in these laboratories has proved the electrometer triode to possess considerable advantages over the standard forms of electrometer as a nullreading voltmeter, and recent publications 2 appear to confirm this The von Halban photometer cannot, however, be satisfactorily modified to allow of the use of an electrometer triode, since the use of a rotating sector introduces a fluctuating grid potential and necessitates the assumption of a linear valve characteristic. To enable an electrometer triode to be used in preference to an electrometer, an alternative method of balancing the currents generated by the measuring and compensating photo-cells must therefore be used, and three such methods have been tried. These were (a) to use one of the cells as a Koch 3 conductor in the grid circuit of the valve, (b) to connect the two cells across a high resistance and vary the voltage applied to the compensating (gas-filled) cell, and (c) to employ a high resistance potentiometer. the three alternative methods, the last has proved the most satisfactory and convenient in practice and has been utilised in the instrument now to be described.

Apart from the advantages accruing from the high sensitivity of the thermionic voltmeter, which permits of the use of a vacuum photo-cell as the actual measuring instrument, the present method possesses other advantages over that of von Halban. Firstly, a greater rapidity in measurement is attainable since the balance point can be quickly and directly determined without the extrapolation which the use of a rotating sector entails. Secondly, the method is not limited by the accuracy of a sector scale and allows of the measurement of high extinctions (approaching 3) for which the sector is unsatisfactory. Finally, the method is independent of the validity of Talbot's law as applied to the measuring photo-cell, and of any assumption regarding the response of a measuring device subject to a fluctuating voltage. The sole assumption is, in fact, that the intensity-current relation for the measuring (vacuum) photocell is a linear one, and this has been shown to be the case over the intensity range involved.

# Optical Arrangement.

The optical arrangement was essentially that of von Halban and is illustrated in Fig. 1. The light source Hg was a quartz mercury lamp burning at 150 volts and 3.8 amp. The beam given by a 5 mm. diaphragm  $D_1$  mounted close to the arc tube was focussed by the quartz lens  $L_1$  of focal length 8 cm. on to the slit of a Hilger monochromator M. Both collimator and telescope slits were of 0.2 mm. width, and the former was cut down to a length of 2 mm. A box B mounted in front of the collimator slit permitted of the insertion of light filters F in the path of the beam.

<sup>&</sup>lt;sup>2</sup> Lees, J. Scientific Instruments, 8, 273, 1931. <sup>3</sup> Koch, Ann. Physik., 39, 705, 1912.

The light issuing from the telescope slit of the monochromator entered the photometer box through a small aperture fitted with a shutter S, and was made parallel by the quartz lens  $L_2$  of focal length 80 cm. at 546  $\mu\mu$ . Immediately behind  $L_2$  the beam was divided by two thin parallel quartz plates P at an angle of 45° to the direction of the beam, which reflected approximately 16 per cent. of the total intensity on to the cathode of the compensating cell  $C_2$ . The direct beam traversed three oval-shaped (9 mm.  $\times$  6 mm.) diaphragms ( $D_2$ ,  $D_3$  and  $D_4$ ) to the measuring cell  $C_1$ . The absorption cell A containing solution or solvent was mounted directly behind  $D_2$ , the distance between  $D_2$  and  $D_3$  being sufficiently great to permit of the use of cells up to 10 cm. in length.

In photo-electric photometry a high monochromatism of the light

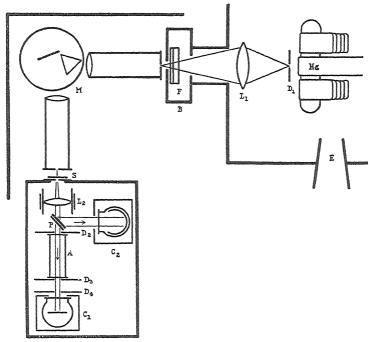


Fig. I.

is essential, especially at wavelengths remote from that of maximum sensitivity for the particular alkali metal used. For this reason, the spectral purity of the beam was further enhanced by the insertion of light filters at B. Suitable filters for the lines 579, 546, 436, 405 and 366  $\mu\mu$  have been described in a previous paper. For the ultra-violet lines below 334  $\mu\mu$ , 5 mm. of 0.0014 per cent. p-nitroso-dimethylaniline in quartz was used. This filter possesses a transmission of 50-70 per cent. over the range 334-248  $\mu\mu$ , and served merely to absorb the blue and violet mercury lines for which the photo-electric response is a maximum. The greater dispersion of the monochromator in the ultra-violet makes less necessary the use of more efficient filters.

The resulting monochromatism has been tested by taking a series

<sup>&</sup>lt;sup>4</sup> Griffith, McKeown and Winn, Trans. Faraday Soc., 29, 369, 1933.

of photographs of the isolated wave-lengths on a Hilger E.3 Spectrograph. No detectable traces of stray radiation were found at any of the fourteen wavelengths listed in Table I. Notwithstanding, it is to be noted that in several cases the light was not strictly monochromatic. Thus the 366  $\mu\mu$  mercury line is actually a group of four lines at 366·33 366·29, 365·48 and 365·02  $\mu\mu$ , and the 579  $\mu\mu$  line a group of two lines at 576·96 and 579·07  $\mu\mu$ . This limits the accuracy of measurement at these wave-lengths when the absorption curve is steep.

### Electrical Arrangement.

The electrical arrangement is shown in Fig. 2. The two photo-cells  $C_1$  and  $C_2$  were Osram Potassium Cells (types UKV6 and UKG7)\* fitted with quartz windows for use in the ultra-violet. The latter (a gas-filled cell) was used as the compensating cell and had a sensitivity at 190 volts of about ten times that of the former (a vacuum cell) which functioned as the measuring cell. Since the compensating cell was illuminated with approximately one-fifth of the intensity incident on the measuring

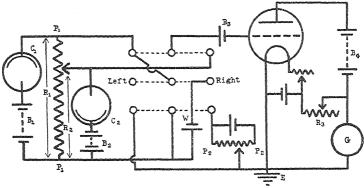


FIG. 2.

cell, the resulting photo-current was approximately twice the maximum photo-current generated by the measuring cell, and it was therefore possible to balance under all conditions. A constant anode potential of 80 volts was used with the vacuum cell ensuring saturation, while from 150-190 volts, according to the wavelength, was applied to the gas-filled cell. The dark current through both cells under these conditions is less than 10  $^{-12}$  amp. and can be neglected.

The potentiometer  $P_1P_1$  of approximate total resistance 10<sup>8</sup> ohms was built from ten 10-megohm and ten 1-megohm fixed resistances and two variable resistances of 0-1 and 0-8 megohm respectively. The two series of resistances were arranged between small mercury cups and connection was made to these by means of a sliding contact. The necessary high insulation was attained by mounting on a sulphur base, and by inserting lengths of Pyrex glass tube in the various operating controls. The three-pole double-throw switch was similarly constructed. The grid

<sup>\*</sup> Note added in proof: The combination of Osram types UKV6 and UNG7 has recently been found to be more satisfactory, especially at wavelengths below  $3^{13} \mu\mu$ .

battery  $B_3$  and the leads from the photo-cells issuing from the photo-meter box were also insulated with sulphur. The insulation has been tested, using a thermionic voltmeter and shown to be above  $10^{13}$  ohms at all points.

The valve used was an electrometer triode obtained from the General Electric Co. Ltd., with a high-grid insulation of  $10^{15}$  ohms and a grid current of less than  $10^{-12}$  amp. The constant current in the anode circuit was neutralised by a "feed-back" from the filament battery through the variable resistance  $R_3$  (0-10,000 ohms) to give zero deflection on the moving coil galvanometer G of sensitivity 3 .  $10^{-8}$  amp. per cm. at 1 m. A change of grid potential of  $10^{-4}$  volt produced a galvanometer deflection of 0.4 cm. The grid circuit of the valve (including the photocells, high-resistance potentiometer, Weston cell W and switch) was earth-screened to shield from extraneous electrical disturbances.

The two illuminated photo-cells are connected across the high resistance potentiometer  $P_1P_1$  and the balance point determined by adjusting  $R_2$  until the potential difference across  $R_1$  is zero. It follows that

$$\frac{I_1}{I_2} = K \frac{i_1}{i_2} = K \frac{R_2}{R_1}.$$

The ratio  $R_2/R_1$  is determined by darkening the photo-cells, connecting a Weston cadmium cell W across  $R_1$ , and measuring the resulting E.M.F. across  $R_2$  by means of the low resistance potentiometer  $P_2P_2$ . If this E.M.F. is E volt, then

$$R_2/R_1 = E/\text{I} \cdot \text{OI 84}$$
  
 $I_1/I_2 = K/\text{I} \cdot \text{OI 84} \times E$ 

and

where K is the ratio of the sensitivities of the two photo-cells. During both of the above operations the valve functions merely as a null-reading voltmeter, the method being therefore independent of the amplification and of the valve characteristic.

The mode of operating is thus to illuminate the photo-cells and to adjust  $P_1P_1$  until no galvanometer deflection occurs on closing <sup>5</sup> the shutter S. The three-pole switch is in its left-hand position during this operation. With S closed, the potentiometer  $P_2P_2$  is then adjusted until no galvanometer deflection occurs on moving the switch from its left to its right-hand position. <sup>6</sup> The E.M.F. given by the potentiometer  $P_2P_2$  (E volts) is then a measure of  $I_1/I_2$ , the ratio of the intensities incident on the two photo-cells. Extinction measurements are thus resolved into the determination of the two values of E corresponding to (i) solvent, and (ii) solution in the absorption cell A in front of the measuring photo-cell. The extinction is then given by

$$\log_{10} \frac{I_0}{I} = \log_{10} \frac{E_1}{E_2}.$$

<sup>6</sup> The galvanometer is momentarily shorted during the transit of the switch.

<sup>&</sup>lt;sup>5</sup> It was found that the photo-current from one (or both) of the cells did not attain its maximum (equilibrium) value until it had been illuminated some 10 seconds, during which period the balance point drifted about 0.5 per cent. The condition of balance was therefore that no galvanometer deflection occurred on closing the shutter S.

# Sensitivity.

Table I. gives the photo-currents generated by the measuring (vacuum) photo-cell at the various wavelengths employed, together with the corresponding changes in grid potential  $(\Delta E_g)$  in the absence of compensating current.

TABLE I.

$\lambda \; (\mu\mu) \; . \qquad . \qquad . \qquad . \ i_1 \; (\mathrm{amp.} \;  imes \; \mathrm{10^{10}}) \; . \ \Delta E_g \; \mathrm{volt} \qquad . \qquad .$	579	546	436 <sup>7</sup>	405	366	334	313
	1·7	3·6	72·4	5·6	18·4	1·3	7·8
	0·017	0·036	0·724	0·056	0·184	o·o13	0·078
$\lambda \; (\mu \mu) \; . \qquad . \qquad . \ i_1 \; ( ext{amp.} \;  imes \;  ext{10}^{10}) \; . \ \Delta E_g \;  ext{volt} \qquad . \ .$	302	297	289	280	265	254	248
	5·I	2·I	0·7	2·0	2·6	1·2	0:7
	0·05I	0·02I	0·007	0·020	0·026	0·012	0:007

The maximum photo-current (at  $\lambda=436~\mu\mu$ ) corresponds to a galvanometer deflection of 3000 cm. and the minimum (at  $\lambda=248~\mu\mu$ ) to one of 30 cm. With a fluctuation of light intensity of  $\pm$  1.5 per cent., the balance point was usually steady at all wavelengths over short intervals of time to the nearest mm., corresponding to a constancy at  $\lambda=436~\mu\mu$  of I in 30,000. Slight variations in the sensitivities of the two photo-cells, however, especially on continuous illumination, reduced this degree of concordance. The following figures give the actual order of constancy obtained:—

 $\lambda=405~\mu\mu$ . 10 readings over a period of 2 hours. Extreme values of E=0.5630-0.5639 volt.  $\lambda=366~\mu\mu$ . 10 readings over a period of 2 hours. Extreme values of E=0.3972-0.3981 volt.

As already indicated, the method is solely dependent upon the assumption that the current-intensity plot of the measuring photo-cell is a linear one. This has been tested by determining the transmission at 436  $\mu\mu$  of two quartz plates (producing a diminution of intensity of about 20 per cent. due to reflection loss) for a series of eight intensities covering the entire range used in extinction measurement. The variation of intensity was effected by inserting a series of neutral filters at B, and the results are recorded in Table II.

TABLE II.

Intensity (relative) . $E_1/E_2$ .	1.000	,	0·300 1·227	0.164				
------------------------------------	-------	---	----------------	-------	--	--	--	--

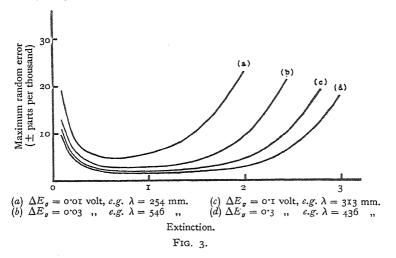
Any deviation of the current-intensity plot from linearity would result in a trend of  $E_1/E_2$  with intensity, and the absence of any variation proves the relation to be strictly linear up to a current of at least 7.10  $^{-9}$  amp.

<sup>&</sup>lt;sup>7</sup> The sensitivity at  $436\mu\mu$  was found to be inconveniently high and was reduced to  $\Delta E_g = 0.3$  volt by decreasing the slit widths of the monochromator.

## Probable Error of Extinction Measurement.

In discussing possible errors, it is necessary to differentiate between random errors in the measurement of extinction by the photo-electric method just described, and systematic errors due to spectral impurity of the isolated light beam.

The random error is determined by the following three factors: (i) slight irregularities in the sensitivities of the photo-cells may result in an error in the balance point of I part in 1000, (ii) the condition of zero voltage across  $P_1P_1$  is only satisfied to  $\pm$  10  $^{-5}$  volt, and (iii) the final potential readings  $E_1$  and  $E_2$  on the potentiometer  $P_2P_2$  may be in error by  $\pm$  5. 10  $^{-5}$  volt. It can be shown that when  $\Delta E_g$  is large, the random error is determined solely by (i) at small extinctions and solely by (iii) at high extinctions; while if  $\Delta E_g$  is small (ii) has the relatively largest effect. Assuming that all errors reinforce one another



in a positive sense in the determination of  $E_1$  and in a negative sense in the determination of  $E_2$ , it follows that

$$\left(\log_{10}\frac{E_{1}}{E_{2}}\right)_{\text{measured}} = \left(\log_{10}\frac{E_{1}}{E_{2}}\right)_{\text{true}} \pm \log_{10} \left(\frac{\mathbf{I} + \mathbf{IO^{-3}} + \frac{\mathbf{IO^{-5}}}{\Delta E_{g}} + \frac{5 \cdot \mathbf{IO^{-5}}}{E_{1}}}{\mathbf{I} - \mathbf{IO^{-3}} - \frac{\mathbf{IO^{-5}} \cdot E_{1}}{\Delta E_{g} \cdot E_{2}} - \frac{5 \cdot \mathbf{IO^{-5}}}{E_{2}}}\right)$$

in which the values of  $\Delta E_g$  are given in Table I. and  $E_1$  is always approximately 0.5 volt. Fig. 3 gives the maximum random error at various extinctions at four typical wavelengths, (a) and (d) representing the extreme cases. It will be seen that at all wave-lengths the maximum error is within  $\pm$  1 per cent. over the range 0.2 to 1.5 of extinction, while at 436  $\mu\mu$  the range extends to an extinction of 2.7. The following figures, on Table III, indicate the precision generally attained.

The absolute accuracy cannot, however, be as high as would appear from the reproducibility, owing to the presence of systematic errors due to non-monochromatism of the light. These errors will be dependent on the conditions applying to a given determination, in particular to the general form of the absorption curve and to the extinction at which

			TA	BLI	3	II.	I.	
λ	=	436	μμ	(con	ıpa	re	curve	(d)).

d(cm.).	$\epsilon = \log_{10} I_0/I$ .	€/d.							
0·2517 0·5020 0·999 2·009	0·3836 0·7651 1·528 3·070	$ \begin{vmatrix} 1.524 \\ 1.524 \\ 1.530 \\ 1.529 \end{vmatrix} $ Mean = 1.526							
	$\lambda = 546 \ \mu\mu \ (\text{compare curve } (b)).$								
2·009 5·029 10•01	0·2681 0·6761 1·340	o·1335 o·1345 o·1339 Mean = o·1339							

the measurement is made. It has been shown  $^8$  that the photo-electric method occasionally gives results which are considerably in error, especially at wavelengths below 300  $\mu\mu$  where the relatively weak intensities of the mercury lines and the low sensitivity of the potassium photocell combine to give a small photo-electric response. Under these conditions, the presence of slight traces of false light of wave-lengths of high photo-electric sensitivity (e.g., 405 and 436  $\mu\mu$ ) may mean that an appreciable fraction of the measured photo-current is resulting from stray radiation with consequent error in the extinction measurement. On this account, a comparison of extinction data obtained by a photoelectric method with data from other sources is generally desirable to prove the absence of any systematic error arising from this cause.

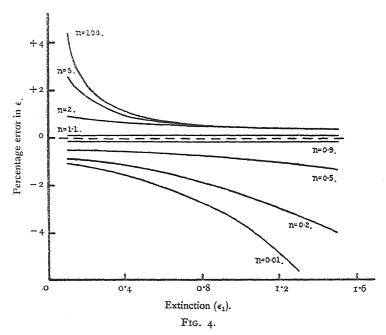
It is, however, possible to estimate the order of accuracy of a particular extinction measurement without resort to such a comparison. The effect of false light is two-fold; (i) it results in an erroneously high or low value of the extinction according to whether the extinction of the false light is greater or less than that of the homogeneous light, and (ii) it produces apparent deviations from Lambert's law. Let  $I_1$  be the intensity of the homogeneous light,  $s_1$  the corresponding sensitivity of the photo-cell and  $\epsilon_1$  the extinction, and let  $I_2$ ,  $s_2$  and  $\epsilon_2$  be the corresponding quantities for the false light. Then defining F as the ratio  $\frac{I_2 s_2}{I_1 s_1}$ , it can be shown that to a first approximation:

Percentage error in 
$$\epsilon_1 = -\frac{100}{\epsilon_1} \log_{10} \left[ 1 + F(10^{\epsilon_1 - \epsilon_2} - 1) \right]$$

Fig. 4 shows how with F=0.01 the error varies with extinction  $(\epsilon_1)$  for various values of the ratio  $\epsilon_2/\epsilon_1$  (=n). For larger values of F, which may easily arise for measurements below 300  $\mu\mu$ , the error is obtained to a first approximation by proportionately increasing the ordinates. It will be seen that a large systematic error may immediately be detected by (apparent) deviations from Lambert's law of similar magnitude over the extinction range 0.2 to 1.5. Further, it follows that

<sup>8</sup> von Halban and Eisenbrand, loc. cit., and Baly, Morton and Riding, Proc. Royal Soc., 113A, 709, 1927.

if a given extinction coefficient is measured at a series of extinctions (by varying the depth of the absorbing layer) from 0.2 to 1.5, and if, apart from random error, the variation over this range does not exceed I per cent., then the systematic error due to false light does not exceed this amount. In this manner, therefore, it is possible to keep a continuous check on the absolute accuracy of measurement.



### Summary.

The paper describes a photo-electric spectrophotometer for the measurement of light absorption in the visible and ultra-violet. A null method employing two photo-cells is used. The photo-currents are balanced across a high resistance potentiometer, an electrometer triode being used as a null-reading amplifying voltmeter. Details of the performance are given and the possible errors discussed.

The author is indebted to Dr. R. O Griffith and Dr. A. McKeown for their interest and advice, and to Imperial Chemical Industries, Ltd., for a grant defraying part of the cost of the investigation.

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# THE KINETICS AND HEAT OF ADSORPTION OF OXYGEN ON PLATINUM.

By E. B. MAXTED AND N. J. HASSID.

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In a previous paper, 1 results have been given which appear to indicate that the differential heat of adsorption of hydrogen on platinum is, over a wide range, independent of the stage of adsorbed concentration at which a given gas increment is added. This is in agreement with the observations of Ward<sup>2</sup> and of Beebe<sup>3</sup> for hydrogen on copper.

The work has now been extended to the adsorption of oxygen, which differs from that of hydrogen in the degree of its reversibility, in that oxygen, when once adsorbed, can only be recovered by degassing at a temperature which is high enough to destroy the adsorbing surface. Since, for this reason, oxygen may be regarded as an adsorbed species the molecules of which are relatively immobile within the surface, it was considered that a re-examination of the differential heat of adsorption of this gas, employing the precautions described in the previous paper, might offer some indication as to whether the constant value observed for hydrogen has its origin in an averaging effect due, for instance, to the mobility of this gas in the adsorbed state.

The differential heat of adsorption of oxygen on platinum has already been measured by Taylor, Kistiakowsky and Perry, 4 who, in almost every case, obtained figures showing a gradual decrease in the heat effect as the adsorbed concentration was increased. Since, however, the calorimeter used was one which gave a progressively decreasing adsorption heat also for hydrogen, it appeared not impossible that the same sources of error which have been discussed by Ward, by Schwabe and Brennecke,<sup>5</sup> and by the authors, might be inherent in the method when applied to oxygen. Employing the precautions previously described, save that desorption experiments could not be undertaken with oxygen on account of the lack of reversibility, constant heat values have been obtained over a wide range, the results being thus analogous to those observed with hydrogen.

The kinetics of the adsorption process have also been studied. general, the logarithm of the adsorbed concentration was found to vary linearly with the logarithm of the time, as observed by Bangham and Burt 6 for other types of adsorption; and, at low initial adsorbed concentrations, at which adsorption takes place relatively rapidly, the adsorption rate was found also to vary directly with the gas pressure.

The apparatus employed was as already described, and included a constant-temperature enclosure of sufficient size to contain all parts in the immediate neighbourhood of the calorimeter. The weight of the

<sup>&</sup>lt;sup>1</sup> Maxted and Hassid, J. Chem. Soc., 3313, 1931.

Ward, Proc. Roy. Soc., 133A, 506, 1931.

Beebe, Trans. Faraday Soc., 28, 761, 1932.

Taylor, Kistiakowsky and Perry, J. Physic. Chem., 34, 799, 1930.

Schwabe and Brennecke, Z. physikal. Chem., 16B, 19, 1932.

<sup>6</sup> Bangham and Burt, Proc. Roy. Soc., 105A, 481, 1924.

platinum black, which was prepared by reducing chloroplatinic acid with an alkaline formate, was IIO g. In order to eliminate oxygen adsorbed during the course of preparation, this was treated in the calorimeter with excess of hydrogen at room temperature, then degassed for

many hours at 100° by means of a combined mercury diffusion and Hyvac

pump.

Small known volumes of oxygen were then added in the usual way, and the heat effect measured. With the specimen of platinum black employed, oxygen was adsorbed quickly and completely up to a stage at which about 5 to 6 c.c. had been added, the pressure after the addition of each increment falling to a value too low to be read on the McLeod gauges.

Neglecting an abnormally high heat effect of 92,500 cals. which was observed for the first increment and which was probably due to reaction of at any rate part of the oxygen added with residual hydrogen, an approximately constant adsorption heat of about 60,000 calories per g. mol. of oxygen was obtained up

TABLE I.

Oxygen Increment, c.c.	Total Adsorp- tion, c.c.	Heat Effect in g. cals. per g. mol. O <sub>2</sub> .
0·221 0·245 0·263 0·308 0·345 0·370 0·383 0·428 0·450 0·481 0·520 0·522	0.22 0.47 0.73 1.04 1.38 1.7; 2.14 2.56 3.01 3.49 4.01 4.54	62,500 61,000 55,000 54,500 60,000 60,500 61,000 58,500 62,500 62,500 62,500 60,000 58,800
	Average	60,000

to a stage at which the adsorption became relatively slow and incomplete. This is shown by the results of Table I.

#### Kinetics of the Reaction.

The kinetics, at advanced stages of adsorption, at which oxygen is taken up relatively slowly, agree with the course found by Bangham and Burt <sup>6</sup> for the general adsorption of gases such as carbon dioxide on glass, according to which straight lines are obtained on plotting the logarithm of the adsorbed concentration against the logarithm of the time. This corresponds with a general equation

$$x = kt^n$$
 . . . (i)

in which x is the adsorbed concentration. The agreement of the adsorption-time curves for oxygen on platinum at stages of adsorption more advanced than those contained in Table I. with this type of equation will be discussed later.

At early stages of adsorption, however, and particularly at low pressures, the rate of adsorption is influenced markedly by the gas pressure at which the adsorption takes place. If, at such initial stages, the rate, as far as the pressure is concerned, be assumed to vary directly as the rate of supply of fresh oxygen molecules—namely directly as the pressure—and if this correcting factor be embodied in the above equation, the resulting expression represents closely the experimentally observed change in adsorbed concentration when both the time and the pressure vary.

Thus, if equation (i) is expressed in the form of its fundamental differential equation

$$\frac{dx}{dt} = k't^m$$

in which m = n-1, we have, on the assumption that the rate varies also directly with the pressure

$$\frac{dx}{dt} = k'pt^m \quad . \qquad . \qquad . \qquad . \qquad (ii)$$

But since x, the adsorption (reduced to N.T.P.), is derived directly from the pressure difference, p may readily be expressed in terms of x by means of the relationship

$$p = \frac{PV - 760x}{V} \qquad . \qquad . \qquad . \qquad (iii)$$

in which P is the initial pressure, p the instantaneous pressure at time, t, and V the volume of the apparatus.

Accordingly

$$\frac{dx}{dt} = k' \frac{PV - 760x}{V} t^m \quad . \tag{iv}$$

In its integrated form, this becomes

$$\frac{1}{a}\log_e \frac{P}{P - ax} = kt^n \quad . \tag{v}$$

in which a is 760/V. Equation (v) thus gives the required relationship between x and t on the basis of a direct variation of the adsorption rate with pressure, as expressed in equation (ii).

The close agreement between the observed and the calculated adsorptions at various times is shown in Table II., which refers to a typical adsorption-time isotherm taken at a stage well before the substantial saturation of the surface. In the measurement cited, the initial adsorbed concentration was about 2 c.c. of oxygen for the II g. of platinum black taken, and the pressure fell continuously from an initial value of 3 mm. to less than 0.2 mm. in the course of a quarter of an hour. The temperature of the measurement was 20° C.

TABLE II.

Time,	Values of $x$ in c.c. at N.T.P.				
	Observed.	Calculated.			
0 1 2 4 6 10 15 ∞	0 0·240 0·302 0·352 0·371 0·380 0·381	0 0·244 0·302 0·352 0·372 0·381 0·388			

TABLE III.

Time, in Days.	Adsorption. C.c. at N.T.P.	Pressure. Mm.
0 2 4·6 15 36 71 105	0 0·75 1·01 1·64 2·27 2·90 3·21	2·8 2·2 2·0 1·5 1·0 0·5 0·25

The experimental values of x for t=2 and t=4 were taken as a basis for the necessary calculation of the values of the constants k and n, and consequently agree exactly with the calculated value; but the very satisfactory agreement for other values of t will be noted: further, the gas increment added amounted to 0.383 c.c., which was completely

adsorbed, while the calculated values for the adsorption have as their

upper limit the closely agreeing value 0.380 c.c.

the above curve rate is plotted graphically, it will be seen that the adsorption-time curve for oxygen on platinum is of a simple continuous type, and that i t thus differs fundamentally from that of hydrogen, in which there is evidently a superimposed relatively rapid and relatively slow adsorption process.

As the adsorbed concentration increases, a stage is reached—with the II g. of platinum black in question at about 5-6 c.c. total adsorption—at which the state

of saturation is such that further adsorption takes place far less rapidly, with a certainly apparent, and possibly real, diminution in the adsorption heat. From this stage of incipient saturation onwards, changes of pressure durnig the adsorption process have far less influence on the adsorption rate; and the course eventually substantially follows equation (1), even if the process is accompanied by not too great a variation in the pressure. This is shown by Curve A of Fig. 1, which corresponds with an isotherm an initial adsorbed oxygen concentration of 8.7

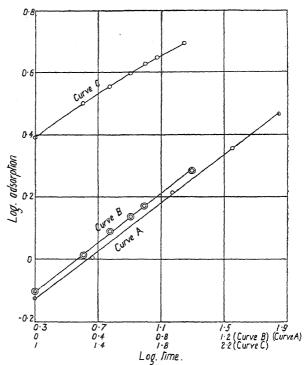


Fig. i.

TABLE IV.

7 // 7		1	T
Initial Oxygen Content, in c.c.	Tempera- ture °C.	Time,	Adsorption, in c.c.
16.2	0	ı hr.	0.76
		2 hrs.	1.03
		3 ,,	1.23
		4 ,,	1.37
		5 ,,	1.48
		10 ,,	1.92
		15 ,,	2.12
		20 ,,	2.24
18.44	100	10 mins	2.46
		20 ,,	3.16
		30 ,,	3.61
		40 ,,	3.97
		50 ,,	4.26
		60 ,,	4.46
		90 ,,	4.92
		120 ,,	5.41
			1

c.c., in which the pressure fell progressively from 2.8 to 0.25 mm. in the course of 105 days, as is shown in Table III.

It will be noted that, under these conditions, the further adsorption is very slow, the time being measured in days; and the substantial following of the simple linear relationship between  $\log x$  and  $\log t$ , irrespective of the fall in pressure, is probably due to the slowness of the process, in that the supply of potentially adsorbable oxygen molecules is always sufficiently great, between the two low pressures studied, to render far less effective the influence of such a pressure change.

Ultimate saturation had, however, even now not yet been attained, especially if the pressure was raised materially; and Table IV. shows the progress of the additional adsorption on raising the oxygen pressure to atmospheric. The first series of results was obtained at 0°, and the second at 100° C.

These results, which are shown diagrammatically in Curves B and C of the figure, may be used to determine the activation energy involved in this slow adsorption process. The activation energy calculated in this way is of the order of 4000 to 5000 calories.

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# CAPILLARY ASCENT OR DEPRESSION OF LIQUIDS IN CYLINDRICAL TUBES.

By Alfred W. Porter.

Received 19th April, 1933.

The recent paper by W. Cawood and H. S. Patterson  $^1$  has not only drawn renewed attention to the need, in manometry, of attending to the *variation* of the capillary correction,  $h_0$ , which accompanies the change of height h of the meniscus, but has supplied an additional table based upon direct experimental measurement. The need of the correction had been well recognised in accurate barometry but many physicochemical determinations of pressure are carried out without any attention being paid to this important source of error.

If mercury behaved according to the simplest assumptions we would observe a single angle of contact for all radii of the containing tube and single values of h and  $h_0$  for any one radius. But mercury sticks to the containing wall even in clean tubes and, when the column rises, the height, h, of the meniscus may increase; the angle of contact then decreases and this is accompanied by a change of the curvature at the summit to which the capillary depression,  $h_0$ , is proportional. On slowly lowering the column the opposite changes occur. The result is that for each height, h, there is a different value of  $h_0$ . The table of Cawood and Patterson gives the values of  $h_0$  which correspond to the values of h for angles of contact which are not stated but which lie mainly between 90° and 45°. For 90° angle the surface of the mercury is a horizontal plane and h and  $h_0$  are zero. The tabulated values depend

of course upon the working substance. In the above paper no mention is made of the value of the surface tension to which they correspond. It will appear in the sequel that it cannot have been much less than 480 dynes per cm., which agrees closely with that obtained for very pure mercury by R. S. Burdon.<sup>2</sup> There is at present, however, an unexplained but fickle variation of this value for mercury, ostensibly pure, down to 440; and this must entail a similar uncertainty of the capillary constant  $\beta^2$  ( $\beta^2 = \sigma/[g(\rho-\rho_0)]$  where  $\sigma=$  surface tension) and a 4 per cent. variation of  $\beta$  on which the tabulated numbers depend. Moreover the effects of slight contamination of the surface by the gases under measurement require examination. Mercury is obviously not an ideal substance for the purpose of manometry though it has undoubtedly outstanding advantages.

Cawood and Patterson make no allusion to the tables of Bashforth and Adams.<sup>3</sup> It is true that these tables need some reduction before they can be used for the present purpose. The variables selected were no doubt the most convenient for calculating the tables but they need to be transformed to others for use in manometry. These tables have been calculated with great precision at the cost of great labour. The values are given to five (or six) significant figures and only show irregularities in the last figure given. Since for the present purpose only three figures are needed no charge of uncertainty can be brought against them. Unfortunately, however, their range is only moderate, the largest diameters included only just overlap the smallest in Cawood and Patterson's table. However they can be made to supply a supplementary table for smaller diameter tubes such as are quite commonly employed for manometers.

I have effected the transformations necessary, obtaining results shown in Figs. I and 2 and Table I. These changes are in part algebraical and involve no loss of accuracy; in part, however, interpolation has been effected graphically and here there is undoubtedly a source of errror; but the figures actually recorded must be very near the truth. They are calculated to suit not mercury alone but any liquid. In other words instead of calculating values of h and  $h_0$  for various values of r, the numbers recorded are the purely numerical quantities  $h/\beta$ ,  $h_0/\beta$  and  $r/\beta$ . They can be used for any substance when the value of  $\beta$  for the substance is known. This involves a little calculation, but this cannot be avoided by any other mode of tabulation unless it is known that  $\beta$  for the liquid used is always the same absolute constant. It is from the last rows which overlap Cawood and Patterson's first rows that one finds that their  $\beta$  is 0·190 cm. or possibly nearer 0·191 cm. and therefore  $\sigma$  is about 480 dynes per cm.

It may not be immediately obvious how the ordinary tables must be altered when a liquid is employed having a different  $\beta$  from that for which they have been *calculated*. If the value  $\sigma=440$  is employed in framing the tables, how will they be changed if  $\sigma=480$  is the value for the mercury which is being *experimentally* used? This is an increase of about 10 per cent. in  $\sigma$ , equivalent to about 5 per cent. in  $\beta$ . As an illustration, let the observed values be

$$r = 0.4 \text{ cm.}, \quad h = 0.2 \text{ cm.}$$

<sup>&</sup>lt;sup>2</sup> Trans. Faraday Soc., 28, 836, 1932.

<sup>&</sup>lt;sup>3</sup> Capillary Action, Camb. Univ. Press, 1883. Out of print.

# 704 CAPILLARY ASCENT OR DEPRESSION OF LIQUIDS

Assume  $\beta_1 = 0.2$  and  $\beta_2 = 0.21$ , so that one is greater by 5 per cent. Using the former we get from the table here given that when

$$\frac{r}{\beta_1} = 2, \frac{h}{\beta_1} = 1$$
, then  $\frac{h_0}{\beta_1} = 0.564$   
 $h_0 = 0.564 \times 2 = 0.1128$  cm.

Using the value  $\beta_2 = 0.21$ , we get when

$$\frac{r}{\beta_2} = 1.90, \frac{h}{\beta_2} = 0.95, \text{ then } \frac{h_0}{\beta_2} = 0.615$$
  
 $\therefore h_0 = 0.615 \times 0.21 = 0.1291 \text{ cm.}$ 

and

TABLE I.

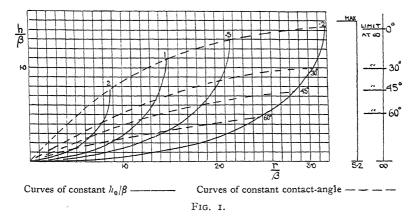
$h/\beta$ .	0.1.	0.2.	0'3.	0.4.	0.5.	o·6.	0.7.	o·8.	0.9.	1.0.	1'1.	1.2.	1.3.	1.4.
						Value	s of I	$r_0/\beta$ .						
56 77 8 9 100 101 102 103 105 105 107 109 200 201 202 203 204 205 207 208 209 301 301 301 301 301 301 301 301 301 301		1·459 1·120 0·892 ·720	1.550 1.265 1.036 0.856 .710 .607 .528 .452	1·540 1·290 1·088 0·917	1.730 1.468 1.250 1.070 0.913 .784 .678 .594 .523 .461 .407 .358 .320 .284	1.600	1.721 1.496 1.291 1.116 0.972 .849	1.164 1.020 0.900 .799 .712 .634 .565 .504 .454 .407 .366 .328 .296	1·200 1·062 0·936 ·836 ·746 ·670 ·603 ·543 ·489 ·441 ·357 ·321 ·290 ·260	·862 ·778 ·700 ·628	0·572 ·517 ·470 ·425 ·384 ·347 ·284 ·258 ·236 ·215	·524 ·476 ·435	·298 ·272 ·250 ·228	0·400 -369 -302 -276 -254 232 -212

Hence the change of 5 per cent. in  $\beta$  in this case increases the value of the depression,  $h_0$  by about 14 per cent. This example shows the great importance of knowing fairly precise values of the data for the liquid before even rough values can be obtained for the depression sought for.

Another example will illustrate the use of the table. On the line for  $r/\beta = 1.2$ , various values are given for  $h_0/\beta$ . These show that for mercury, if  $\beta = .2$ , the depression may vary from 0 to 0.272 cm. in a tube of radius 0.24 cm. according to the angle of contact at which the liquid is held. If the meniscus height is not observed there is therefore

an uncertainty of 2.7 mm. in the pressure that is being measured. (Cawood and Patterson found that it was easier to produce angles of contact from 90° to 45° than for the rest of the range; I understand that the values in their table correspond mainly to this semi-range and moreover they deal with much wider tubes.) It may safely be said that when pressures are being measured manometrically the observations are of no value unless the height of the meniscus is read at the same time as the height of the mercury column.

There is an additional point to which attention should be called. When the angle of contact is 0° the value of  $h/\beta$  is greater at  $r/\beta=3\cdot165$  than it is at  $r/\beta=$  infinity. Since it is rising at the former point it must reach a maximum in between. The maximum is known to lie in the region (or not much beyond that) to which Cawood and Patterson's data apply. For angles of contact greater than 0° there is still evidence of maxima, but nothing is known as to their positions except that they lie in a region beyond the range of the Bashforth and Adams tables. I have shown the existence of these maxima on Fig. 2 in an exceedingly tentative way by means of dotted lines. The certain facts are the lines



of constant contact angle from which the dotted extensions arise and the terminal points on the horizontal axis of co-ordinates, i.e., at  $r/\beta = \infty$ .

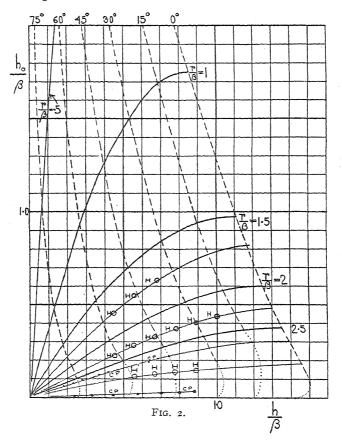
The same values of  $h/\beta$  may be found therefore for two different values of  $r/\beta$  and any given angle of contact, one on each side of the maximum. This raises no difficulty in the use of tables drawn up with this fact recognised. But it may account for some of the irregularity which has been found when using tubes more than 19 mm. diameter in the case of mercury. It must certainly be disconcerting to find h unexpectedly getting smaller as r increases.

In Fig. 1 the general relation between the variables is shown. The continuous curves represent (to scale) the shapes of the contours for the different radii and angles of contact.

For mercury the curves require to be inverted. The accurate information on which they have been constructed has been available in the Bashforth and Adams tables since 1883, i.e., fifty years ago. Each continuous curve represents a selected value of  $h_0/\beta$  upon which the curvature at the vertex depends; the value of  $h_0/\beta$  for any curve is given at the upper end of the curve. The discontinuous curves mark

off the terminations of these surfaces for different angles of contact. Thus when  $h_0/\beta=0.5$  and the angle of contact is 30° the value of  $r/\beta$  is about 2.05. For mercury when the angle of contact is 45° (the normal value)  $h_0/\beta$  would be 0.5 when  $r/\beta=1.84$ . The figure serves for illustrative purposes to show the general relation between the variables, but it is on too small a scale to be trusted for accurate measurements. The table must be consulted for the latter purpose.

If  $h_0/\beta$  is plotted against  $h/\beta$  (Fig. 2) for any one radius the curves obtained are roughly hyperbolic becoming horizontal on top. This is because angles of contact down to zero are included. In this respect



they are like Heuse's, while Cawood and Patterson deal mainly with the range 90°-45° which corresponds approximately to the asymptote of the curve through the origin. This throws light on the reason for Heuse's observations (if represented approximately by a straight line) giving a line which does not go through the origin, h=0,  $h_0=0$ . I have represented by small circles (marked H), on Fig. 2, Heuse's tabulated values for three different radii assuming their value of  $\beta$  as being approximately 0·18. It will be seen that their values follow quite comfortably the general scheme of the diagram. Cawood and Patterson rather precipitately object to them because a straight line through them

does not pass through the origin. The diagram, however, shows clearly that straight line extrapolation is not expected to be valid. All the constant-radius lines on Fig. 2 are concave toward the horizontal axis. The only one which would be straight is the limiting one at  $r=\infty$  and this coincides with the horizontal axis itself. Cawood and Patterson found that their line for radius 0.526 cm. was slightly curved toward the h axis. I have shown their actual data as solid dots (marked CP) on Fig. 2; it will be seen that their line also falls in with the general scheme. For the higher radii and the limited range of angle of contact a straight line extrapolation is probably satisfactory especially when we consider the decreasing importance of the capillary depression in these cases. I have shown in the same way their data for the widest tube they employed together with a straight line through them; but it must be remembered that this line must become horizontal when the contact angle is zero.

It is scarcely necessary to add that the scale of the diagram has been selected to suit the range of the Bashforth and Adams data. The chief object of this paper has been to put these data forward. The scale is not suited to the higher radius curves.

The following short table for the value of  $\beta$  for mercury will be found useful when the acceleration due to gravity at London is taken as 981.2 cm. per sec.<sup>2</sup> and density of mercury at 20° C. is 13.55 gms./cm<sup>3</sup>.:—

Surface Tension.	440.	450.	460.	470.	480.	
β	0.1820	0.1840	0.1860	0.1880	0.1900	

# EXPERIMENTS ON THE CRYSTALLISATION OF INGOTS.

By R. G. Heggie, Ph.D.

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In the manufacture of steel, the properties of the finished product are known to be determined in large degree by the structure of the ingot which is cast from the molten metal. This is especially the case in regard to the non-metallic inclusions which are invariably present, and to the segregation of soluble impurities, which tend to accumulate in those portions which are the last to freeze. The importance of this problem has led to many isolated investigations, and a systematic study of segregation has been undertaken by the Heterogeneity of Ingots Committee of the Iron and Steel Institute and the Iron and Steel Industrial Research Council, the voluminous reports of which contain a large amount of valuable information.

The work described in the present paper was carried out in the Metallurgical Department of Sheffield University under the supervision of Professor C. H. Desch, and in the later stages under that of Professor J. H. Andrew, and was undertaken with a view to an approach towards a solution of the problem from a rather different angle. The heterogeneity of ingots depends in large measure on the course taken by the

process of crystallisation, and the following experiments were directed towards a determination of the conditions under which columnar crystals are formed. These are the crystals which, in most ingots, grow in a direction approximately perpendicular to the walls of the mould. The region in which they terminate, being replaced by equiaxed crystals of random orientation, is the seat of much of the segregation usually observed, and is thus of special interest.

The substances used were commercial stearic acid and tin metal. The former is well known through the work of A. W. and H. Brearley (Ingots and Ingot Moulds) and other workers, and its similarity of crystallisation to that of steel is well known. Tin was used as a representative pure metal in order to illustrate the variation between a pure metal and a mixture of two substances.

That motion has a very definite effect on the resulting structure of an ingot has been clearly shown by A. Hultgren and others, and therefore it was decided to eliminate this factor as far as possible, and to deal with ingot masses passing from the liquid to the solid state without the introduction of motion, either from teeming or stirring, while freezing was taking place, with the exception of one case in which the effect of motion was required.

# Experiments with Commercial Stearic Acid.

The first series of experiments made with stearic acid consisted of a number of chilled ingots made in the following manner:—

The mould used was made of ordinary tinplate and was about 4 inches high, and square in section, tapering from \( \frac{3}{8} \) inch side at the top to  $I_{\frac{1}{N}}$  inch side at the base. Timplate was used for the mould so that its resistance to heat transfer would be negligible compared with that of the stearic acid.

A I-litre beaker was filled with water and heated by a Bunsen burner. The mould, filled with stearic acid, was immersed in this beaker so that less than  $\frac{1}{2}$  inch of the open end projected above the surface of the water. A finely graduated thermometer was suspended in such a manner that the bulb was as near the geometrical centre of the molten stearic acid as possible. Another thermometer was used for regulating the temperature of the water in the beaker. A second beaker of the same capacity containing water at room temperature was kept close at hand.

The water in the first beaker was heated until it had reached the required temperature above the freezing-point of the stearic acid, and was kept there for some time. The water in the beaker and the stearic acid in the mould were kept well stirred until they were at a uniform temperature throughout. The stirring of the acid was then stopped and several minutes were allowed for it to come to rest. The first beaker was then quickly replaced by the second beaker containing cold water, the water in this beaker being kept constantly stirred while frequent additions of cold water were made to it in order to keep its temperature. as nearly as possible, at that of the room. The ingot was allowed to freeze under these conditions while the heat changes at its centre were noted. When completely frozen, the ingot was knocked out, sectioned down the median plane, etched and examined. This experiment was carried out for a series of initial temperatures of 85° C., 75° C., 65° C., 57° C. and 55° C.

The results of these experiments are shown in the photograph, Fig. 1,

the initial temperature decreasing from left to right. The columnar character of the ingots will be noted even when the initial temperature of the stearic acid before chilling is only slightly above its freezing-point. The cooling curve obtained is similar to B in Fig. 2, showing a prolonged horizontal arrest at, or near, the liquidus of the mixture. Similar experiments carried out with cold bath temperatures of 25° C. and 35° C. respectively, and the same initial series of temperatures yielded similar results.

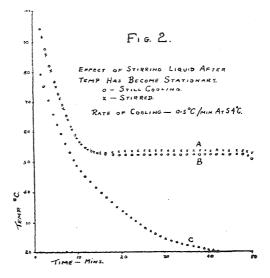
These experiments show that the change from the columnar to the equi-axial type of crystallisation is dependent on neither the initial temperature of the substance of the ingot, nor upon the temperature

of the cold bath which is inducing freezing.

A second series of experiments was designed in order to determine the effect of a gradual reduction of the rate of cooling on the crystalline structure of ingots of stearic acid, motion during freezing being again eliminated. The pro-

cedure was as follows:—

A 1-litre beaker, filled with water, was placed on a stand over a Bunsen burner. The water in the beaker was kept well stirred by means of a motordriven propeller. ingot mould, as previously described, was suspended the in beaker so as to be almost completely immersed, and a thermometer suspended with its bulb as near the geometric centre of the mould as possible. A second thermometer



was suspended with its bulb in the water in the beaker and as close to the outer surface of the mould as was convenient.

A reservoir placed on a shelf above the bench supplied a steady stream of water to the beaker during the experiment, the rate of flow being adjusted by means of taps so that any required rate of cooling could be obtained. In later experiments, in order to obtain slower rates of cooling than could be obtained by means of a flow of water, the reservoir was disconnected, and ordinary air cooling adopted. Still slower rates were obtained by lagging the beaker with cotton wool, and finally by freezing an ingot in a Dewar flask originally filled with hot water.

The water in the beaker was raised to a temperature considerably above the freezing range of the stearic acid while being stirred continuously. The mould immersed in the water was then filled with molten stearic acid, and this was also stirred until it had assumed the even temperature of the bath. The Bunsen burner was then removed, and the flow of cooling water from the reservoir turned on at a definite rate.

The temperatures on both thermometers were noted at regular intervals, and the difference between these, neglecting mould effect, gave the total difference in temperature between the centre and the outside of the stearic acid. Six different cooling rates were taken as stated above. The ingots when completely frozen were knocked out, sectioned, and etched as in the previous experiments.

The results are shown in the photograph, Fig. 3, a decrease in the cooling rate being shown as we proceed from left to right. The small pieces on which the ingots were standing were broken sections from the remaining halves of the ingots. It will be noticed that the "definiteness" of the columnar crystals becomes less and less from left to right, and in the fifth ingot from the left (beaker lagged with cotton wool), they are very few and short, and their direction of growth is almost at random, suggesting that they are more or less accidental formations. In the sixth ingot (Dewar flask), they are entirely absent, and the crystallisation is equi-axial throughout.

In character, the cooling curves obtained in this series are similar to those of the chilled ingot series as shown at B and C, Fig. 2, the curve C which shows the outside temperature of the ingot, yielding no promise of information.

These results are corroborated by those obtained on small circular ingots. The so-called "chill" crystals are noticeably absent both from these and from the chilled ingots. The "chill" crystal layer here referred to is the outer finely equi-axed zone which is found on the surface of an ingot.

The following experiment illustrates the effect of a small amount of motion on the liquid centre of a freezing ingot when this centre has reached the under-cooled state. The apparatus used in this experiment was that used previously. A slight oscillatory motion was given to the thermometer suspended in the mould, care being taken in each test that the thermometer bulb did not touch the dendrites growing inwards from the sides. A duplicate set of ingots was made in which no motion was introduced in order to illustrate the resulting difference in structure. Two pairs of these ingots are shown in Fig. 4. It will be seen that motion has caused the cessation of columnar crystalline growth, and has resulted in a very fine equi-axial crystallisation.

The cooling curves obtained from all the foregoing experiments seemed to show that a state of dynamic heat balance is set up in a freezing mass of stearic acid, and this would seem to corroborate the results which B. Matuschka had obtained on plain carbon and nickel-chrome steels. By dynamic heat balance is meant that the latent heat evolved in freezing at any particular moment is just sufficient to balance the heat removed at the surface of the mould. Therefore we have a mass of liquid at the centre of the mould, each unit of which contains the same total heat, but the mass of this liquid is decreasing as the solid wall advances towards the centre of the ingot. It was decided to carry out a series of experiments designed to give curves on stearic acid equivalent to those which Matuschka had obtained on steel, so that a more direct comparison could be made.

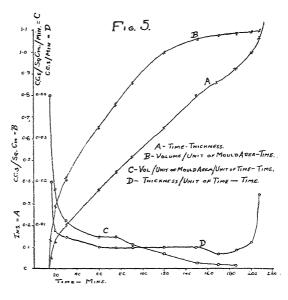
A square-section mould of height 8 inches, and average side-length 2 inches, made from thin sheet steel was used. The stearic acid was heated to 80° C. and poured into the mould, being stirred continuously until the temperature had fallen to 65° C. It was then allowed to become still and to fall to the freezing temperature. Time measurements were

commenced when the acid reached 65° C., and at a definite time from the commencement of each experiment the ingot was bled, the volume of the cavity measured by means of water, and the shell knocked out. This shell was then sectioned and its linear thickness measured at a definite position on the ingot halfway down. Twelve different times of freezing were taken so that fairly accurate curves might be obtained.

As the time for the complete freezing of such an ingot is in the neighbourhood of 4-5 hours, and since no feeder heads were used, the cooling effect on the exposed surface of the acid was allowed for by considering the total surface of the ingot as the cooling surface when constructing the (volume per unit of mould area)-(time) curves.

The curves obtained are shown in Fig. 5. Curve A represents the time-thickness curve, and its relationship to those obtained by Matuschka is quite obvious. Curve B represents the (volume per unit of mould area)-(time) curve, and its relation to that of Matuschka is also re-

markable. The resemblance is brought out even more clearly by curves C and D, the differentials of curves A and В. These were obtained by direct measurement from curves A and B, and it will be noted that they correspond with those of Matuschka even in their irregularities. Fig. 6 shows series of ingot sections obtained in these experiments. The first three ingots of the series are not shown since the walls were rather thin, and the shells proved too fragile for preserva-



tion, a portion of the third ingot shell is, however, shown.

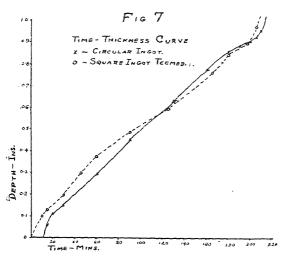
When the great difference in physical properties between stearic acid and steel is considered, it will be realis that these curves are definitely functions of ingot freezing, and that Matuschka is probably in error when he remarks that the probable cause of the difference between the curves which he obtained with plain carbon and alloy steels is a difference in their physical properties.

Similar experiments carried out with a mould of exactly half the linear dimensions of the previous mould gave curves of an exactly similar nature, and thus the actual mass of the ingot would not seem to be a factor affecting the forms of the curves. Another series of experiments was carried out with a mould of circular cross-section. This mould was made of thin steel sheeting, and was 8 inches in height with a mean diameter of 2 inches. It was not thought necessary in this case to plot more than the time-thickness curve since it is perfectly obvious

that all these curves are inter-related. The results of these experiments are shown by the full line in Fig. 7. The change of geometrical shape of the mould certainly does seem to have caused a slight modification of the curve. Thus the first inflection of the curve occurs earlier than in the case of the square ingot, and the range of dynamic heat balance seems to be longer, with the second inflection occurring a little later than before.

An additional and important point to be noted in these experiments is the fact that since the metallic container and the stearic acid are cooling together, there is very little likelihood of an air gap, which has been regarded as important for steel ingots, appearing between the ingot and the mould, and therefore this effect will not interfere with the curves.

The dotted line in Fig. 7 shows the curve obtained from a square ingot when teeming was resorted to. In this case the measurement of the wall thickness is far less accurate than in any of the previous experiments, in which the wall surface was clearly defined as a plane.

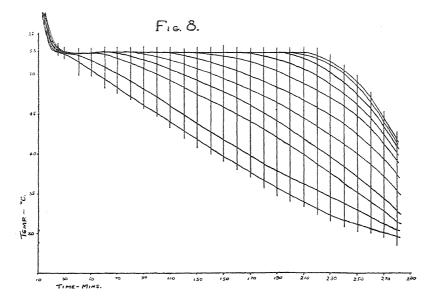


In the teeming experiments, an average for wall thickness was taken.

The foregoing experiment raised the interesting point as to whether a more complete thermal investigation of the freezing of an ingot of stearic acid could be carried out. Attempts were therefore made to obtain temperature gradient curves in ingot mass during This was freezing. carried out as follows, using multiple

thermo-couples. The couples, twelve in number, were spaced from the centre to the outside of the ingot, and consisted of 38G constantan, and 42G black enamel coated copper wires. The constantan wire, owing to its low thermal conductivity, gave very little trouble with regard to heat conduction, but it was found necessary to reduce the copper wire to the smallest dimensions compatible with sufficient robustness to withstand usage. The black enamel coating acted as an additional safeguard against heat removal. In addition, the couples were carried up from the middle of the mould to the surface of the stearic acid with the copper wire enclosed inside a very finely drawn glass tube, the constantan wire being taken up outside this tube. These tubes were placed as nearly as could be judged along the isothermal planes of the ingot. In this way fairly consistent results were obtained. The cold junction was common to all leads, and consisted of a common joint immersed in a Dewar flask containing melting ice. The copper leads were carried to a commutator switch, and common leads were carried both from this and the cold junction to a galvanometer adjusted so as to give a deflection of approximately 1.5 cms. per 1° with a I metre scale. The couples were calibrated in the usual way, and no trouble was experienced with parasitic e.m.f.'s.

The procedure of these experiments was standardised on that of the preceding ones so that the results might be comparable. The couples were suspended in the mould at the position where previous time-thickness measurements had been made. The stearic acid was heated in a separate vessel to a temperature just above 80° C. On falling to 80° C. it was poured into the mould, and was stirred continuously until its temperature fell to 65° C. Stirring was then discontinued, time and temperature readings were commenced, while the stearic acid was allowed to become still, and finally, freeze. The readings were taken at half-minute intervals, commencing with the outer couple and progressing inwards until all couples had been read, and then beginning again at the outer couple. Each couple was thus read once every



6 minutes, and since the total time of freezing was between 4 and 5 hours, this yielded about 50 or 60 points on each curve, and therefore the curves are considered quite reliable.

The resulting cooling curves are shown in Fig. 8. To find the simultaneous temperatures on the series of twelve curves, it is now only necessary to erect an ordinate at the particular time from the commencement of the experiment at which the temperature gradient is required.

In order to construct the temperature gradient curves it is necessary to know the exact distance between the thermo-couples, and this was determined by sectioning the ingot near the couples, dissolving the stearic acid away with ether until the couples just showed, and then measuring the intervals between them accurately.

The temperature gradient curves were then constructed and are shown in Fig. 9. In general character, they are very similar to those

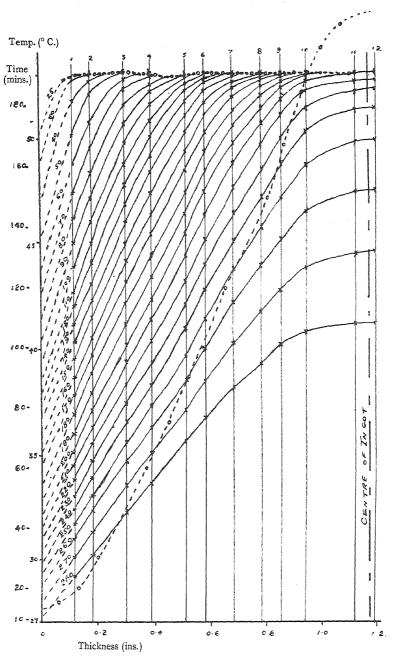


Fig. 9.—Square ingot.

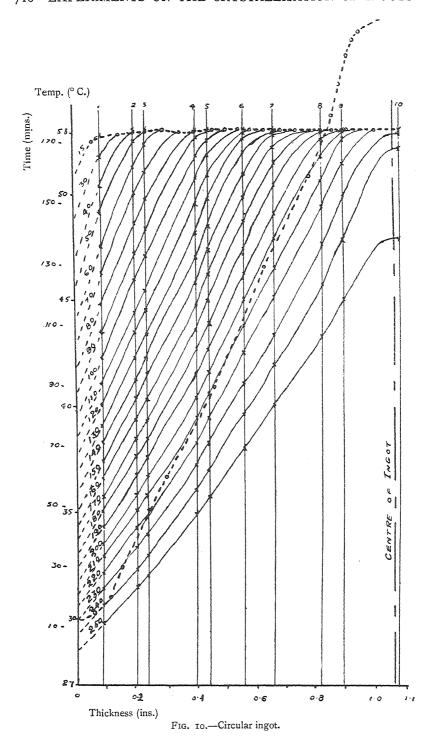
calculated by Saito and Lightfoot for steel, but they show a definite arrest at or near the liquidus temperature as was to be expected from the results of all the previous experimental work. Since the conditions of this and the previous experiment had been standardised, their results can be combined. The time-thickness curve is shown as a dotted line

passing upward from left to right across the graph.

Since the time-thickness curve is based on the length of the columnar crystals, and the position of measurement both of temperature and of thickness is the same in both cases, the two can obviously be combined to yield a curve which is shown as a thick dotted line at about the liquidus level of the stearic acid. The temperature gradient curve at 60 minutes from the commencement of the experiment may be chosen as an example. The curve gives the temperature at any depth from the surface at a certain point on the ingot at the given moment, but it gives no indication of the position of the growing face. The time-thickness curve, however, gives this indication, and the thickness at the time 60 minutes on this curve yields the necessary information. By drawing an ordinate on the temperature gradient diagram corresponding to this thickness or depth, this ordinate will cut the temperature gradient curve at a certain point, and the abscissa through this point will yield the temperature of the growing face at that particular instant. By doing this for every temperature gradient curve, we obtain the curve indicated. This is actually the (temperature)-(length of columnar crystal) curve, that is, it apparently gives the temperature of the points of these crystals at any time during freezing. It will be noticed that this curve rises gradually from below the liquidus temperature until it reaches it or approaches it very closely at a point corresponding with the first inflection on the time-thickness curve. It then proceeds to fall off again slightly, and this seems to correspond with the formation of a number of so-called "free" crystals as can be seen by comparison with the photograph, Fig 6. The curve then again approaches the liquidus temperature, and the formation of further "free" crystals seems to be arrested, while those already formed are gradually surrounded by the thickening walls.

These results are again supported by those obtained on circular ingots in a similar manner. The curves are shown in Fig. 10, and it will be noticed that the (temperature)-(length of columnar crystal) curve differs from that of the square ingot only in that it shows a less complete recovery initially, before again falling off slightly. This seems to be marked by a slightly greater tendency to deposit "free" crystals over this range, as will be seen from the photograph of the ingot sections, Fig. 11. This appears to be a stage when slight undercooling is present throughout the liquid stearic acid, and corresponds to a period immediately following the first inflection on the time-thickness curve. The curve resulting from a series of teemed ingots is shown in Fig. 12, the irregularity of which is due to the difficulty of accurate measurement in this particular case, but the general relationship to the other curves can be seen.

Fig. 13 shows a typical ingot structure as obtained in the teeming experiments. The outer layer of acid has assumed the columnar form of crystallisation, this being followed by a wide layer of equi-axial crystallisation, and towards the centre of the ingot, a return to the columnar form. Attention is drawn to the fact that this would seem to show a relationship between this phenomenon and the inflections on the time-thickness



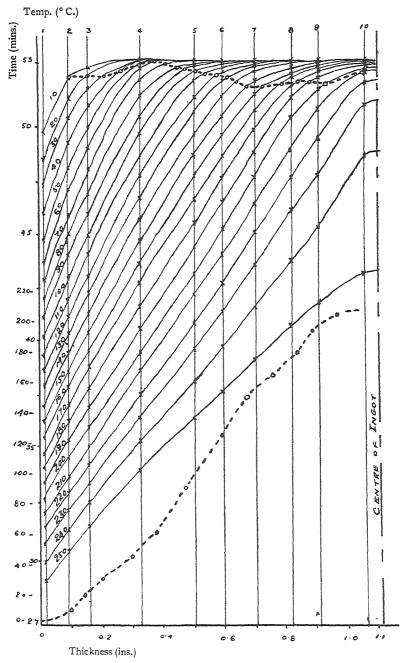


Fig. 12.—Square ingot, teemed.

curves previously obtained. That is, with rapid freezing, the formation of the columnar type of crystal, and with slow freezing, the equi-axial type. It may also be significant that the columnar crystallisation seems to occur on a rising (temperature)—(length of columnar crystal) curve.

#### Experiments with Metallic Tin.

The experiments on stearic acid having proved so interesting, it was decided to repeat some of them on a pure substance in order to observe its behaviour under similar conditions. Tin was chosen as a suitable substance for experiment.

The first series of experiments consisted in making a number of chilled ingots as in the case of stearic acid. The mould used was of thin sheet steel of  $3\frac{1}{2}$  inches depth, and of circular cross-section with a mean diameter of I inch, slightly tapered from top to bottom. Two other sheet metal vessels were used, one containing cold mercury to act as a cold bath, and the other containing mercury at a temperature slightly above the melting-point of tin depending on the particular test which was being carried out. Both of these vessels and the mould were provided with stirring rods and thermometers. The procedure was as follows. The mould was filled with molten tin, and placed in the hot bath. The mercury in the bath and the tin in the mould were then thoroughly stirred until they reached a uniform temperature throughout. The mould was then quickly removed, and plunged into the cold bath with as little disturbance as possible. The mercury in the cold bath was then kept thoroughly agitated, and additions of cold mercury made to prevent the temperature from rising. When completely frozen the ingot of tin was knocked out, sectioned and etched. The initial temperatures of the tin before plunging into the cold bath were, as nearly as possible, 0°-1° C., 3°-4° C., and 6°-7° C., above its freezing-point. The temperature of the cold bath was 50° C.

The results of these experiments are shown in the photograph, Fig. 14, the ingots being columnar throughout except in the case of the first ingot in each series. In this case there is little doubt that the molten tin was not above its melting-point when plunged into the cold bath, and that nuclei of solid tin were already present. The ingots plunged into the cold bath only a few degrees higher are columnar throughout, and this seems to show that the initial temperature of the metal has no effect on the change of the form of crystallisation as long as it is definitely above the freezing-point when chilled.

These results were confirmed by similar experiments using cold bath temperatures of 100° C., 150° C. and 200° C. respectively, no difference being noticeable in any of these as regards general structure. Therefore, the temperature of the cold bath does not seem to be a factor causing any sudden change in structure.

To make a series of tin ingots, using adjusted cooling rates, was rather more difficult than in the case of stearic acid. The following apparatus was constructed. It consisted essentially of a rectangular sheet metal vessel 4 inches in depth, and width 3 inches, with a total length of 7 inches. This vessel was divided into two compartments by means of a thin sheet metal partition, the ingot compartment being 4½ inches long, and the cooling compartment 2½ inches long. The whole was wound with nichrome wire, and lagged so as to form a furnace with an open top. The larger compartment was then filled with rammed moulding sand to a depth of I inch, and a wooden pattern of the ingot to be made placed on the moulding sand with one face against the partition wall. More moulding sand was then rammed round this pattern until the compartment was completely filled. The pattern was then carefully removed, the current switched on to a low heat, and the sand carefully dried and then baked. The mould was then filled with molten tin to within I inch of the top, and this covered with a I inch layer of fine dry silica sand. This yielded an ingot 2 inches deep, 2 inches wide and I inch thick, and being lagged on five of its six sides, would be representative of a small section removed from the side of a large ingot. The remaining side of the mass of tin is, of course, the cooling surface, and the various rates of cooling were induced on this as follows:—

(a) Air cooling.

(b) Cooling together with mercury in the smaller compartment.

(c) Cooling as in (a) and (b) with a thin sand layer over the cooling surface.

(d) Chilling by pouring cold mercury into the smaller compartment. (e) Chilling by pouring cold water into the smaller compartment.

(f) Cooling continuously by low melting-point alloy in the smaller compartment by additions of further alloy kept at a temperature of 150° C.

During the experiments in which a liquid cooling medium was used, this was agitated continuously by means of a motor stirrer. These various means of cooling gave a wide range of cooling rates to the tin.

The ingots obtained in each and every case were columnar in character throughout, these crystals commencing at the cooling face, and growing throughout the mass, the only variation noticeable being the width of the columnar crystals formed, these being wider the slower the cooling rate. Fig. 15 shows two typical ingots obtained by this means. It is quite clear that in this case at least, the columnar form of crystallisation is the only form that can be obtained.

In order to obtain still lower cooling rates, a diatomaceous brick was taken and hollowed out to a certain depth. A cover was cut from the same material. The brick was then strongly heated on the inside by means of a Bunsen burner, the cover being heated simultaneously. The tin, meantime, was also melted in a crucible. When sufficiently heated, the hollow brick was placed on a refractory stand, almost filled with molten tin considerably above its melting-point, and the cover placed over it. The mass of tin was allowed to freeze under these very slow cooling conditions, and when completely frozen was removed, sectioned and etched.

The result is shown in Fig. 16, and it will be seen that only a single crystal of tin has been produced. That is, we still have the columnar form of crystallisation persisting at this very slow cooling rate.

It appears obvious from the above experiments that in a pure substance such as tin, the columnar form of crystallisation is the normal form at all cooling rates, and that equi-axial crystallisation will only be obtained by the introduction of motion in some form or other.

#### Conclusions.

Let us now consider more fully the freezing of an ingot of stearic acid. The initial solid layer is deposited on the surface of the mould at a temperature considerably below the liquidus temperature of the mixture, and thus the initial freezing is very rapid. A layer of stearic acid of irregular surface through which a temperature gradient and concentration gradient existed, corresponding with the interval between liquidus and solidus for that particular mixture, must be present. The width of this layer will be determined by the rate of heat removal at any particular moment. Therefore it will gradually become wider until a state of dynamic heat balance is set up and will then remain constant. Meantime, the temperature of the mass of liquid in the centre of the mould falls to the liquidus temperature or just below it. That is, instead of having a gradual fall in temperature of the central liquid over the range between the liquidus and the solidus, we have this gradient occurring in a narrow layer travelling inwards just in front of the solid wall, while the remainder of the liquid remains at or just below the liquidus temperature. Therefore, if there is any tendency towards equi-axial crystallisation, it will be most evident in this layer, when at its widest, or in other words, when a state of dynamic heat balance has been set up. This period occurs just after the first inflection on the time-thickness curve, and the experimental evidence seems to support this. But if columnar crystallisation has already commenced, any particle tending to separate in this freezing layer will be within the sphere of influence of a dendrite which is growing inwards from the side of the mould, and therefore will tend to deposit on that dendrite. is, to obtain equi-axial crystallisation in such an ingot, this form of crystallisation would have to be initiated at the surface of the ingot, with a width of freezing layer which would enable any particle tending to separate to be outside the sphere of influence of any particle which had already separated. In this way, an ingot would be obtained which would show equi-axial crystallisation throughout.

It is obvious that in the case of a pure substance this would not apply, since the width of any such freezing layer would be zero as it has no freezing range of temperature. It is also obvious that the width of any such freezing layer would be directly dependent on the width of the freezing range of temperature of an alloy. That is, each alloy (referring to solid solution types) would have a definite critical cooling rate which would yield ingots with equi-axial crystallisation throughout, but a similar alloy having a slightly wider freezing range of temperature would have a slightly higher critical cooling rate to yield the same

resulting structure.

That this is so, is supported by experimental work which has been carried out on tin-cadmium alloys over the solid solution range of the diagram. The diagram of these alloys is very similar indeed to that of the iron-cementite alloys, and that is the reason for its choice.

The existence of a sphere of influence in the neighbourhood of a growing dendrite has been mentioned, and some force appears to be exerted by a dendrite on a particle separating from the liquid near it. The character of this force is, however, not well understood, and the only suggestion which is offered on this point is that it may possibly be due to a power possessed by a dendrite of orientating a separating particle in its neighbourhood.

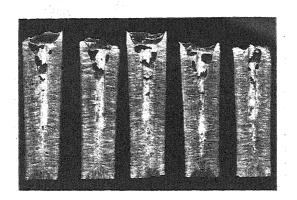


Fig. 1.

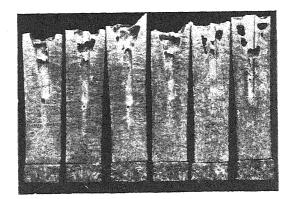


Fig. 3.

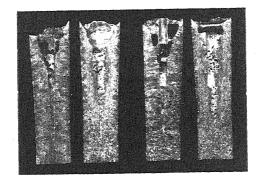


Fig. 4. [See fage 708.

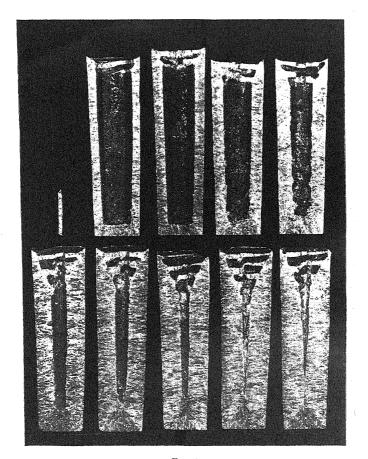
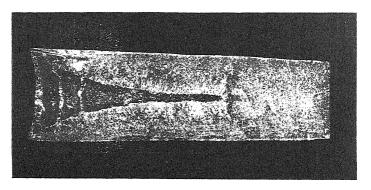


Fig. 6.

See page 711.



F16. 13.

[See page 715.

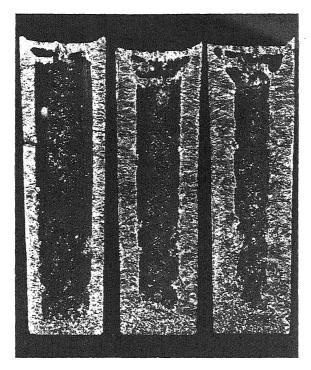


Fig. 11. [See page 715.

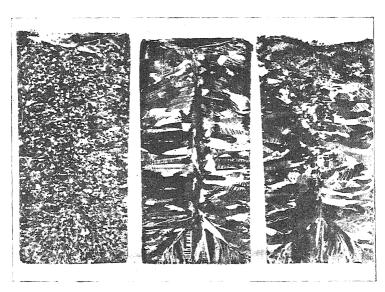


Fig. 14.

[See page 718.

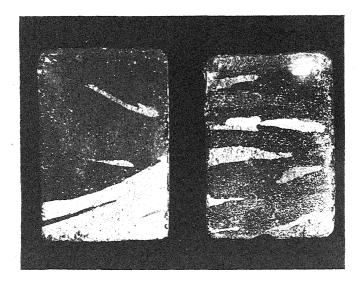


Fig. 15.

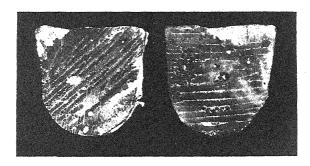


Fig. 16.

[See page 719

## Summary.

The following conclusions seem to be warranted by the results of the foregoing experiments:-

(a) Under the simplest conditions of freezing, that is, without the introduction of motion due to teeming, columnar crystallisation will persist

to the centre of the ingot.

(b) A solid solution has a limiting critical cooling rate below which the equi-axial form of crystallisation will take place throughout the ingot, and above which, under "still" conditions of freezing, only columnar crystallisation will be obtained.

(c) This limiting critical cooling rate is a function of the width of the

freezing range of temperature of the solid solution.

(d) In a pure substance, under "still" conditions of freezing, only columnar crystallisation can be obtained owing to the fact that the width of the freezing range of temperature is zero.

(e) Motion has a definite effect on the change from columnar to equiaxial crystallisation, probably having its greatest effect when a state of

dynamic heat balance has been set up.

(f) The time-thickness and other curves obtained on stearic acid confirm those obtained by Matuschka on steel, and support the assumption of a range of dynamic heat balance.

(g) The temperature gradient curves obtained resemble those calculated by Saito and Lightfoot, and show definitely that for stearic acid, a state

of dynamic heat balance does exist.

(h) Under-cooling does not necessarily produce equi-axial crystallisation in an ingot of stearic acid, nor does it appear to change the columnar form of crystallisation under normal conditions.

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### REVIEWS OF BOOKS.

The History of the Microscope. By REGINALD S. CLAY, D.Sc., F.Inst.P. and THOMAS H. COURT. (Messrs. Charles Griffin & Co., Ltd., 1932. Pp. xiv + 266, 18 × 25 cms.; 164 illustrations. Price 30s. net.)

This is essentially a volume for the expert collector. For him it contains the results of a critical examination of over 7000 historical microscopes of various dates. "The cataloguing for sale of the extensive set of microscopes formed by the late Sir Frank Crisp afforded an unique opportunity of settling doubtful points and of confirming the conclusions already arrived at by the examination previously made of other instruments." The microscopes actually illustrated here include 102 in the "Court Collection" in the Science Museum at South Kensington, 18 in the "Clay Collection" and others in the Science Museum, the collections of the Royal Microscopical Society and of many Continental museums.

To the collector and the historical student the book will be an invaluable aid toward understanding the gradual development which this important instrument for research has undergone.

To the general student of science the substance of the book will be a revelation. Rapid invention is a modern phase. The use of glass bulbs filled with water to produce magnification was known to the ancients, but the effect appears to have been attributed to the medium, not to the shape. The first mention of a lens is attributed to the Arabian Alhazen (962-1038). Roger Bacon had acquaintance with the properties of lens-shaped bodies (convex and concave). Spectacles appear to have been invented about 1299 (p. 5). The first reference to combinations (microscopes, telescopes) is by Thomas Digges (Pantometria, 1571), who attributes such combinations to his father. Much more definite is the description by William Bourne (M.S. Lansd. Mus. Brit. 121) of "the glasse that ys grounde, beeynge of very cleare stuffe, and of a good largenes and placed so that the beame dothe come thorowe, and so reseaved into a very large concave lookinge glasse, that yt will shewe the thinge of a marvellous largeness, in manner uncredable to bee beleeved of the common people" (p. 6).

It is a long journey from these early beginnings to the present microscope. Indeed it is so long that the description of the last step to the *achromatic* microscope has had to be postponed to a later volume.

All who are interested in instruments will find the present book a mine of delight. To the collector the possession of it will be an essential.

Faraday and His Metallurgical Researches. By SIR R. A. HADFIELD, Bt., D.Sc., D.Met., F.R.S. (London: Chapman & Hall, Ltd, 1931. 21s. net.)

Faraday has justly been described as one of the greatest experimental philosophers the world has ever known, and many books and papers have been written extolling his discoveries in physics and chemistry. Little has been said in the past, however, about his metallurgical work, in spite of the fact that an investigation into the effects of alloys on steel was his first major research and one to which he devoted nearly six years' work. The importance of this metallurgical work has probably been overlooked because it was years in advance of metallurgical

knowledge and hence led to no striking results of immediate practical value, although it aroused a great deal of interest at the time. Its true importance, however, has been demonstrated in a strikingly interesting manner by Sir Robert Hadfield in the book which he has written on Faraday and his metallurgical researches.

In the early part of last century, metallurgy was an art carried on largely according to tradition handed down from generation to generation, and developing slowly the meanwhile. True, there had been notable discoveries, as for example the production of crucible steel by Huntsman about the middle of the previous century. Steel, however, was being produced only in relatively small quantities and it would appear that the merits of Huntsman's steel were not always fully appreciated. For example, Stodart, Faraday's collaborator in metallurgical work, apparently regarded wootz, made in India, as superior to any steel produced in this country or elsewhere in Europe though nothing wasiknown as to why wootz should possess this superiority. The idea, therefore, of improving the properties of a metal such as steel, about which so little was really known, partook of the nature of a voyage into unknown regions and was a worthy subject for a prince among experimenters. That the investigation yielded no results of immediate practical value was not the fault of the experimenter; it was due to the art of steelmaking at the time being not nearly sufficiently advanced to profit by his work.

Possibly the greatest interest in Sir Robert's book centres round the examination he has made of a large number of Faraday's actual steels. The greater part of these, some seventy-nine specimens, were discovered in a small deal box in the storerooms of the Royal Institution. Nine further samples were also obtained from Mr. A. Evelyn Barnard, and these proved particularly interesting as they included some with high contents of rhodium, platinum, and palladium, alloys which were known to have been prepared but which were missing from the samples found at the Royal Institution. The author's expression of thanks to Mr. Barnard and to the managers of the Royal Institution for their kindness in allowing these century old samples to be completely examined with all the resources of a modern research laboratory, will be endorsed by all metallurgists who have been thus enabled to have a still more detailed account than Faraday himself could possibly give, of what are undoubtedly the earliest alloy steels made.

Apart from the detailed account of the investigations on these samples, investigations which, it may be noted, required a great deal of skill because the amount of material available was so small, the author has given brief sketches of the various people who were likely to have influenced to any extent Faraday's metallurgical outlook. Prominent among the men described in this chapter, fittingly entitled "The Stage and the Dramatis Personae," is James Stodart who was co-author with Faraday of the two most important metallurgical papers. Stodart was a maker of surgical instruments, razors, and other cutlery, and he it was who most probably made arrangements for the large scale experiments which were carried out at the works of Messrs. Sanderson at Sheffield, presumably after the examination of the earlier samples, which had been made by Faraday in a small wind furnace at the Royal Institution, had led him and Stodart to believe that their results were such as to justify trials on a more practical scale. It seems likely that Stodart's death in 1823 severed the contact which Faraday had had through him with the production of steel on a commercial scale and may have been a potent reason for the somewhat abrupt cessation of Faraday's metallurgical work. The latter had undoubtedly reached a scale for which the resources of his laboratory at the Royal Institution were inadequate, and inability to obtain further large scale trials would be a serious bar to further research. Whatever the cause, Faraday apparently in 1824 abandoned his metallurgical research.

What induced Faraday in the first instance to undertake investigations on steel is only a matter of conjecture. Possibly the fact that his father was a smith and that he himself, as he says in one of his letters, loved a smith's shop and anything relating to smithery made metallurgical work attractive. He would undoubtedly be familiar with Stodart's preference for wootz, and possibly this knowledge had fired him with a desire to produce a still better material for cutlery and similar purposes. It is of special interest to know that he had definitely in mind the production of a steel which would not corrode and actually he produced alloys, containing large amounts of platinum and rhodium, which were strikingly successful in this direction, though at a prohibitive cost. He experimented with chromium steels, but his experiments did not lead him to suspect that the addition of large amounts of chromium to steel would produce a material having such resistance to corrosion as to justify its modern name of "stainless steel."

In describing Faraday's metallurgical work, Sir Robert Hadfield had a fascinating subject. He has dealt with it in an equally fascinating manner and, in establishing beyond all doubt the fact that Faraday was a pioneer in metallurgy as well as in chemistry and physics, he has also added to his own reputation. Apart from the actual metallurgical examination of Faraday's samples, in itself an investigation of no little difficulty, the biographical part of the author's work, dealing as it does not only with Faraday but also with those with whom he came in contact and who may have influenced his outlook on metals, has involved a great deal of patient investigation. The thanks of all those interested in metallurgical science are due to the author for his account of a most notable episode in the history of that science.

J. H. G. M.

The General Properties of Matter. By Professor F. H. Newman and V. H. L. SEARLE. (Second edition, Ernest Benn, Ltd., 1932. Pp. 388. Price 18s. net.)

The fact that a second edition of this book (which was first issued in 1928) has been required is a sufficient indication that it is fulfilling a want. The chapters include Gravitation, Gyroscopic Motion, Elasticity, Surface Tension, Viscosity Kinetic Theory and Osmosis.

The changes from the first edition are mainly concerned with the correction of such few matters as appeared open to criticism. The reviewer's only criticism is that, though excellently produced, the price might with advantage have been less.

Electrons and Waves. By Professor H. Stanley Allen, F.R.S. (London: Macmillan & Co., Ltd., 1932. Pp. ix and 336. Price 8s. 6d.)

This work is based on lectures given at St. Andrew's to teachers attending a summer school. It therefore gives an account of modern ideas which is readily comprehensible by those who are not specialists. It deals with relativity, the quantum theory, crystal analysis, the origin of spectra, de Broglie's theory and wave mechanics.

. It provides an admirable summary sufficient to enable the reader to understand the main principles actuating much of modern thought in physics.

Elektrolyte. By H. FALKENHAGEN. (Hirzel, 1932; pp. xvi + 346; 25 × 17.5 cm.; 24.80 M. bound, 23 M. paper.)

This volume, of which the author is one of the foremost workers in the field with which he deals, is written from an essentially contemporary standpoint, and should be, for some years at all events, the standard book on the subject.

Although the work of former years, in as far as it leads up to present views, is dealt with adequately, very little attention is paid to past attempts to account for, or to express empirically, the "anomalies" of strong electrolytes. And whilst the nature of dilute solutions of strong electrolytes, now so satisfactorily explained in terms of the theory which had its origins with Milner and which has owed its development, above all, to Debye, is discussed very fully, the treatment of more concentrated solutions is very much briefer. For example, the subject of ionic solvation, including its relation to mobility and to transference data, receives no systematic attention. The discussion of viscosity is confined to recent work on dilute electrolytes, and the subject of diffusion is omitted. It will be clear that the author has a well-defined point of view; he regards the theory of Debye and recent developments arising out of that theory as standing in quite a different category from any other work bearing on the nature of strong electrolytes, and many will agree with him. In emphasis of what has been written, it may be added that, whilst there are in the index ten lines of references to Debye, followed by Falkenhagen (5), Hückel (5), Onsager (4), Arrhenius (3), Bjerrum (3), La Mer (3), Nernst (3), and Randall (3), there is no mention of any of Baborovsky, Bein, Bousfield, Buchböck, v. Hevesy, Lindemann, Oholm, Remy, Rudolphi or Steele.

Within these self-imposed limits, the treatment of the subject is complete, logical and satisfying. Preliminaries, including the thermodynamical theory of ideally dilute solutions, and the classical Arrhenius theory of electrolytic dissociation, with its justified application to weak electrolytes, are disposed of in the first three short chapters. Then follows a discussion of the experimentally found thermodynamic anomalies of strong electrolytes, and of their formal expression by G. N. Lewis in terms of the conception of activity. Conductivity data are next dealt with and, after a short interlude devoted to older attempts to account for the difference between strong and weak electrolytes, the heart of the book is reached in chapters 7-10 (153 pp.), dealing with the Debye theory, and its detailed application to ionic equilibria, heats of dilution and electrolytic conduction, all in dilute solution. The effects of frequency and of intensity of electric field on conductivity are discussed (experimental methods are not omitted), and recent work on viscosity is briefly reviewed.

Under the heading of concentrated solutions, which the author does not yet regard as capable of satisfactory theoretical treatment, the theories of ionic association receive attention, as also the work of Davies and of Wien on true degrees of dissociation. There is brief reference to the optical behaviour of strong electrolytes (including the Raman effect), and to Brönsted's theory of specific ionic interaction, and the volume closes with a chapter devoted to the statistical investigations of Fowler and of Kramers. The recent quantum-mechanical treatment of electrode processes by Gurney and Fowler appeared too late for inclusion, whilst the subjects of colloidal electrolytes and of reaction kinetics (Brönsted) are omitted, as still being in their preliminary stages of development.

Throughout, the author does not attempt to slur over any of the mathematical difficulties, and most readers will find the book to require very close application. This is, however, inevitable in the case of any strict treatment of the subject, and the book is strongly recommended to all those who are interested in such a treatment. It should be added that Professor Debye has written a preface, and attention may be drawn to the relatively low price of publication of what must have been an expensive volume to produce.

The Free Energies of Some Organic Compounds. By G. S. Parks and H. M. Huffmann. A.C.S. Monograph Series Chemical Catalog Co. Inc. New York, U.S.A. \$4.50. Pp. 234, with appendices.

This monograph is very welcome at the present time. With the development of physical chemical methods and the fuller recognition of their importance in industrial processes a great impetus has been given to research in this field, partly at least with the object of eventual technical application. It is only natural that the hitherto closed and thickly wooded garden of organic chemistry should be trespassed on by the invading physical chemists, and with the now partly realisable potentialities in both coal and oil ever present with us, the possibilities of gathering rare and refreshing fruit must be explored. No safer guide through the jungle of compounds and reactions can be found than the principles of thermodynamics, for the light given out by the lamps of electron pressure and electronic polarisation is at present too feeble to guide any but the boldest, and we may say the best. Before it is possible to ride we must walk, and the study of reaction kinetics, interesting as it is, cannot be regarded as complete until equilibria are known. For the determination of the free energies of compounds it is necessary to know both the heat of reaction as well as the specific heats and chemical constants of the species involved. This book may well be taken as a blow to the pride of twentieth century chemistry for we find revealed our complete ignorance of these fundamental data. Thanks to international co-operation, exact values for the heats of combustion of substances are now appearing, but the experimental values for the specific heats of all gases (especially at high temperatures), with the exception of the monatomic gases and of hydrogen, diverge so widely from the band spectroscopic values that such work should be put in hand at once. The authors are to be congratulated not only in collecting together the data available in such a concise and critically presented form, but in having included in the volume the various electrometric methods which have been suggested for the determination of free energies in organic systems. These methods are undoubtedly capable of extension, and the simplicity of the methods, as well as the accuracy attainable, render them doubly attractive.

The book, like others in this series, is well printed and bound.

ERIC K. RIDEAL.

Annual Tables of Constants (A.T.C.), and Numerical Data, Chemical, Physical, Biological and Technological. Vol. VIII., 2 parts (1927-28), 2706 pp. (22 cm./28 cm.). Price 500 frs. Vol. IX. (1929), 1607 pp. and Index, 124 pp. (22 cm./28 cm.). Price 400 frs. (Gauthier-Villars & Co., Paris. McGraw Hill Book Co., New York.)

These more than 4000 pages bring up the *Tables Annuelles* to the data for 1929. It is pleasing to note that with Vol. IX. the annual publication, which was part of the original intention, is resumed. This huge task could not have been carried through except under the auspices of such an international body as that founded by the Seventh Congress of Applied Chemistry at its meeting in London in 1909. We congratulate them on the success of their enterprise.

It is impossible for us in this notice to do more than enumerate the chief sections of these volumes. In Vol. VIII., Pt. I., 77 pages are devoted to Rotatory Power and 557 pages to Emission Spectra. In Part II. 368 pages collect the data of Absorption Spectra; 165 pages those on Solubility; 67 pages the data of Velocities of Reaction; 71 pages those of Electromotive Forces; 86 pages deal with the structure of matter as revealed by X-rays; 74 pages with Organic Chemistry, and 91 pages with Metallurgy. All these data are for the years 1927-28. In Vol. IX. special attention is called to the new chapters on

Emission Spectra (pp. 279), Absorption Spectra (pp. 140), Photography, Geophysics, Radio Electricity, Explosions and Combustion of Gaseous Mixtures. These data are for the year 1929. A Table des Matières is given, in a separate volume, to No. IX. and it is intended to continue the publication of these indices so as to facilitate reference. Readers may be reminded that the tables are now published with all the explanatory matter in both French and English in the same volume. Many of the sections are freely illustrated with scaled diagrams; for example the chapter on absorption spectra contains 128 such diagrams for solutions.

The fullness and accuracy of the information provided in these Tables deserves great praise. It is only *very* occasionally that we come across doubtful specifications in those sections with which we are specially acquainted. It should be further noted that the Secretariat place themselves at the disposal of readers desirous of obtaining fuller information concerning data contained in periodicals to which they have no access.

All information can be obtained from the General Secretary, M. Charles Marie, D.-ès-Sc., 9 rue de Bagneux, Paris VIe.

Report on Band-Spectra of Diatomic Molecules. By W. JEVONS, D.Sc. (Published by The Physical Society, London. Pp. 308. Price 17s. 6d. net.)

For a rather long time a comprehensive book on molecular spectra was lacking, and it was only at the end of 1931 that the now well-known book of Weizel appeared. This was written from a rather theoretical point of view. A book written from an experimental and more elementary point of view was still lacking. This gap has now been filled by Dr. Jevons' new book.

Thanks to the work of a great many investigators the structure of diatomic molecules and their spectra are now known in most of their essential features. This however is not at all the case for polyatomic molecules and the investigation of these is just now in a state of very rapid development. The same may be said on the question of valency, both for diatomic and polyatomic molecules. It must therefore in some respects be regarded as an advantage of the present book that these topics have been omitted, since this prevents the book from rapidly getting out of date. The theory of band spectra of diatomic molecules is already so extended and the experimental material so vast that, in spite of these omissions, the book is of quite appreciable size.

Dr. Jevons deals first with the experimental side of the problem. He provides a valuable summary of the different sources in which bands of diatomic molecules have been observed and then a description of the simplest cases of band spectra. It is only in the later chapters of the book that the more complicated structures are discussed. This procedure seems to be very well suited for the beginner. In this respect the very numerous practical examples for theoretical deductions, the very good reproductions of spectrograms and the large number of diagrams and tables are also extremely useful.

It seems however that the book is even more useful to those already working on band spectroscopic problems because of the extreme thoroughness with which all of the finer details of the structure of band spectra have been collected. With the same thoroughness nearly all available examples for every single case are discussed. In addition, in an appendix, Jevons gives a very well arranged table of the constants of all known electronic levels of diatomic molecules with a corresponding bibliography. Numerous tests have convinced the reviewer of the completeness and reliability of this table. The value of this collection of data cannot be overestimated.

In recent years the investigation of band spectra has become of increasing

importance to chemistry. Not only have a number of fundamental molecular constants of the stable diatomic gases (dissociation energy, nuclear distance, vibrational frequency, energy of excited states, etc.) been determined from their band spectra, but also the investigation of those diatomic molecules which are not chemically stable, i.e. free radicals (their occurence in discharges, flames, etc., and their molecular constants) has been made possible. Even radicals previously unknown to the chemist have been found. Furthermore a number of chemical elementary reactions (e.g. the photochemical primary process) have been cleared up. This book, therefore, will be equally invaluable to chemists, especially physical chemists, not only because of the complete table of all molecular constants but also because it forms a plain and comprehensive survey of the whole subject of diatomic band spectra.

G. HERZBERG.

Atom and Cosmos. By Professor Hans Reichenbach (University of Berlin). English Translation by Edward S Allen, Associate Professor of Mathematics, Iowa State College. (London: George Allen & Unwin, Ltd. Pp. 300. Illustrated. Price 8s. 6d.)

The book of which this is a translation is an outgrowth of lectures which the author broadcasted in Berlin during the winter of 1929-1930. The aim of the broadcasting was to present physical knowledge to non-physicists. In its book form the matter has been much altered and expanded, but its aim is still the same. The author claims not to presuppose "any knowledge of the kind taught in schools nor does he desire to furnish any such knowledge." He deals with Space and Time, Light and Radiation, Matter, and Philosophical consequences. He endeavours to expound those views which are characteristic of the developments taking place at the present time. As the translator remarks the book gives evidence of the high quality of the material which is broadcast in Berlin and which is desired by a German audience.

Needless to say some small degree of acquaintance with questions of science and philosophy is, after all, necessary for a reader to go through the book with much profit. The author will appeal most to those who have a general acquaintance with the philosophical aspects of Newton's work but who have not yet become convinced of the truth of (or even acquainted with the details of) the modern theory of relativity.

The exposition is very lucidly carried on. Now and then the author has allowed himself to be tempted into by-paths. For example, it was scarcely necessary to introduce the Goethe-Newton controversy concerning the production of colours by prisms: its introduction only serves to interfere with the general argument. Such wandering, however, very seldom occurs.

The translator (aided by his wife) appears to have performed his task exceedingly well. There is none of the stumbling so frequently found in translations and the discussion is a sound and very readable exposition of the modern changes of view in physics.

L'Azéotropisme. La Tension de Vapeur des Mélanges de Liquides. Bibliographie. By Maurice Lecat. (Maurice Lamertin, Bruxelles. Pp. viii + 135. Price: 12 Belgas.)

# THE INFLUENCE OF THE COMPOSITION AND ACIDITY OF THE ELECTROLYTE ON THE CHARACTERISTICS OF NICKEL DEPOSITS.

By D. J. Macnaughtan, G. E. Gardam, and R. A. F. Hammond.

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The following is an account of the third part of a general investigation into the causes and prevention of pitting in electrodeposited nickel carried out in the Research Department, Woolwich, for the Electrodeposition Research Committee of the Department of Scientific and Industrial Research.

The results of the first two parts of this investigation have been given in a previous publication.¹ Typical examples of the defect were described and it was shown that pitting is caused by the screening effect of bubbles of gas (probably of hydrogen) which adhere to the cathode face during deposition; the formation of hydrogen bubbles may be localised by the presence of imperfections in the surface of the basis metal and thus give rise to a variety of pitting termed "basis-metal pitting." In the case of cathodes possessing a uniform surface, however, pitting occurs solely as a result of the condition of the solution ("solution-pitting"), and it was concluded that this type of pitting results from the presence of impurities in the solution.

In more recent investigations, however, cases of solution pitting have been observed in highly purified solutions; the intensity of pitting and the  $p_{\rm H}$  range in which it occurred were found to be influenced by the composition of the solution. It was also observed that variations in solution composition and  $p_{\rm H}$  exerted a marked effect on the hardness, microstructure, cathode efficiency and appearance of the deposits, and it became clear that the explanation of these effects could only be obtained by a systematic study of the deposits obtained under carefully controlled conditions in which the influence of the different constituents of a typical nickel depositing solution could be separately examined. The results of this study, given in the following report, throw new light on the mechanism of nickel deposition and explain the occurrence of pitting in solutions of high purity.

#### PART I. EXPERIMENTAL.

The experimental work consisted in the preparation of salts and anodes of high purity and the use of these materials in the production of deposits for comparison of the effects of changes in solution  $p_{\rm H}$  and composition and the appearance, cathode efficiency, hardness and microstructure of the deposits.

1" The Causes and Prevention of Pitting in Electrodeposited Nickel," D. J Macnaughtan and A. W. Hothersall, Trans. Faraday Soc., 24, 497, 1928.

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An endeavour was made to eliminate all sources of impurity both initially in the preparation of the materials, and also during the process of producing the deposits, when care was taken to exclude dust from the depositing solutions. There appeared to be some doubt, however, about the effect of air dissolved in the solution; it would appear that this might lead to the production of pits in the deposit by causing the formation of bubbles on the cathode surface. This possibility was carefully investigated in a series of experiments in which nickel depositing solutions of composition NSB. KC (see Table II.) were saturated with air at a low temperature and were subsequently electrolysed at a higher temperature. Although a considerable number of bubbles of gas were liberated on the cathode, no increased pitting was observed. These experiments were repeated using hydrogen instead of air with the same result. Finally experiments were carried out in which, in one case, bubbles of air injected through a nickel gauze anode and in another case bubbles of oxygen formed by electrolysis with a platinum anode, were caused to impinge on the cathode face, but no increase in pitting was observed.

It was concluded from the above experiments that such pitting as occurs is primarily due to hydrogen gas formed at the cathode face as a result of the discharge of hydrogen ions.

#### Preparation of Anodes and Salts.

(a) Preparation of Salts of High Purity.—In view of the necessity of eliminating uncertain factors caused by the presence of impurities in the solutions, the purest salts obtainable, usually of "A.R." quality, were used, and these were in some cases further purified by treatments previously described.2 The analysis of the nickel salts used is given in Table I.

				Nickel Sulphate, NiSO <sub>1</sub> . 7H <sub>2</sub> O.	Nickel Chloride, NiCl <sub>2</sub> . 6H <sub>2</sub> O.
Nickel		•		20.8 per cent.	22.5 per cent.
Cobalt				0.09 ,,	Nil.
Iron				0.001 ,,	0.004 ,,
Zinc				0.01 ,,	0.01 ,,
Copper				0.001 ,,	trace
Mangane	ese		.	< 0.001 ,,	_
Alkali m	etals		.	Nil	trace

TABLE I .- ANALYSES OF THE NICKEL SALTS USED.

(b) Preparation of Anodes of High Purity.—Electrodeposited nickel anodes of high purity were prepared in a manner similar to that previously described 3 with the exception that a glass container with a sintered glass base was used in place of the ebonite container.

#### Composition of the Solutions.

In order to facilitate reference to the various solutions a scheme of lettering has been adopted in which anions and cations (other than hydrogen and hydroxyl ions) have been denoted by single letters, viz., N = nickel, S = sulphate, B = borate (in all cases added as boric acid), K = potassium, C = chloride. Thus a solution containing nickel sulphate, boric acid and potassium chloride is referred to as NSB. KC.

A. W. Hothersall, Trans. Faraday Soc., 24, 387, 1928.

<sup>&</sup>lt;sup>2</sup> "The Influence of Acidity of the Electrolyte on the Structure and Hardness of Electrodeposited Nickel," D. J. Macnaughtan and R. A. F. Hammond Trans. Faraday Soc., 27, 633, 1931.

3"The Hardness of Electrodeposited Nickel," D. J. Macnaughtan and

	Grammes per Litre.							
Key Reference of Solution.	Nickel Sulphate, NiSO <sub>4</sub> . 7H <sub>2</sub> O.	Nickel Chloride, NiCl <sub>2</sub> . 6H <sub>2</sub> O.	Chloride, Chloride,		Boric Acid, H <sub>3</sub> BO <sub>3</sub> .			
Solutions buffered with Boric Acid.—								
NSB . KC * NSB . C NSB . K NSB	240 — 210 30·3 240 — 240 —		— — —	22.3	30 30 30 30			
Unbuffered solutions.—								
NS.KC NS.C NS.K NS	240 210 240 240	30.3	19 — —	22.3				

TABLE II.—Composition of Solutions.

#### Preparation of the Solutions.

In order that the range of acidity to be investigated in the various solutions should be as wide as possible, it was necessary to ensure that the solutions as prepared should all possess the highest  $p_H$  attainable. In the cases of solutions free from boric acid, this object was achieved by prolonged boiling of the salts dissolved in distilled water with a slight excess of highly pure nickel hydroxide suspension. The solution was then cooled, filtered and made up to volume with distilled water.

This process could not be followed in preparing the solutions containing boric acid, as on boiling such solutions hydrolysis takes place thus limiting the maximum  $p_{\rm H}$  attainable to about 5.1. A special procedure was therefore adopted in which the salts and the boric acid were treated separately by boiling with pure nickel hydroxide. The solution of the salts was then allowed to become quite cold, when the hot nickel borate solution was added to it in a fine stream with constant stirring. Filtration followed by adjustment to volume completed the process.

In this way it was found possible to prepare clear solutions at  $p_{\rm H}$ values considerably in excess of the true equilibrium. The solutions thus prepared were, however, found to be unstable and tended to become turbid owing to the precipitation of basic material with consequent fall in  $p_{\rm H}$  even at normal temperatures. Particular difficulty was encountered in preparing solutions NSB, NSB. K and NSB. C at a high p<sub>H</sub> for this reason.

# Experimental Procedure.

Two separate series of deposits were produced (1) thin deposits for visual examination, (2) thick deposits for hardness tests and examination of microstructure; the cathode efficiency of nickel deposition was measured in all cases and for this purpose a copper coulometer was connected in series with the nickel bath, the coulometer cathode being of such a size as to maintain copper deposition at a current density of 10 amps. per sq. ft.

1. Thin Deposits for Visual Examination.—The solutions, 5 litres in volume, were contained in round glass jars, 8 inches in diameter, and were heated to a temperature of 35° ± 1.0° C. A single nickel anode, approximately  $4\frac{1}{2} \times 2$  inches in size, prepared as described, was suspended

<sup>\*</sup> This solution has been denoted in previous published work 2 4 by the symbol " N.'

in the solution. In the case of the solutions free from chloride it was found necessary to surround the anode with a porous pot which was filled with solution to which had been added an excess of pure nickel hydroxide suspension, as otherwise the low anode efficiency effected a rapid change in the  $p_{\rm H}$  of the solution. Cylindrical porous pots were employed and were first ignited at a bright red heat in a muffle furnace and subsequently soaked in successive quantities of distilled water until the soluble matter had been entirely removed (as revealed by the absence of residue on evaporation of a sample of the water to dryness).

The cathodes consisted of thin copper sheets,  $1\frac{1}{4} \times 2$  inches in size. They were carefully cleaned and copper coated in an acid copper sulphate solution to a thickness of 0.0005 inch. They were then washed, dried and weighed and subsequently prepared for deposition by cathodic treatment for a few seconds in an alkaline solution followed by a momentary dip in 10 per cent. sulphuric acid solution—a procedure which did not involve

any appreciable change of weight.4

One cathode was used in each experiment and was arranged at right angles to the plane of the anode so as to secure an equal distribution of

current on each face.

The  $p_{\rm H}$  value of the solutions was reduced in stages by the addition of pure sulphuric acid, the acidity being maintained within  $\pm$  0·05  $p_{\rm H}$  units of the stated values in the case of the buffered solutions, and within  $\pm$  0·1  $p_{\rm H}$  units (approximately) in the case of the unbuffered solutions, any upward tendency being corrected by the addition of acid. Duplicate deposits were made at each  $p_{\rm H}$  value, the intervals of  $p_{\rm H}$  between successive stages being determined partly by the ease with which the  $p_{\rm H}$  could be controlled and partly by the degree to which change in  $p_{\rm H}$  was expected, from preliminary observations, to alter the characteristics of the deposits.

Other conditions of deposition were as follows:-

Cathode current density 11 amps. per sq. ft. (1.2 amps./sq. dm.). Duration of deposition 2 hours (equivalent to a thickness of deposit of approx. 0.0015 in. (0.04 mm.)).

On removal from the solution the cathodes were rinsed in distilled water followed by alcohol, dried in an air oven at 80° C., cooled and weighed.

2. Thick Deposits for Hardness Testing and Micro-examination.— This part of the work was confined to the buffered solutions containing boric acid, since the  $p_{\rm H}$  of the unbuffered solutions could not be controlled sufficiently closely throughout the prolonged period of deposition necessary to produce a thickness of deposit adequate for Brinell hardness testing.

The solutions were contained in round glass jars supported in a thermostatically controlled water bath, four purified nickel anodes hung on nickel wires being arranged symmetrically around the internal periphery of the jars. Three litres of solution were used in the case of NSB. KC and NSB. C

and 5 litres in the case of NSB. K and NSB.

The cathodes which were hung centrally in the jars, consisted of pieces of hexagonal mild steel rod which had previously been coated with a layer of electrodeposited copper oot inch in thickness. The cathodes measured r.5 inch in length and o.625 inch across the flats in the case of solutions NSB. KC and NSB. C, and I.125 inch in length and o.25 inch across the flats in the case of solutions NSB. K and NSB, the smaller size being employed in conjunction with a larger volume of solution in order to minimise changes of acidity by reducing the amount of current flowing in relation to the volume of solution. The cathodes were prepared for deposition by the method previously described.

4" The Influence of Small Amounts of Chromic Acid and Chromium Sulphate on the Electrodeposition of Nickel," D. J. Macnaughtan and R. A. F. Hammond, Trans. Faraday Soc., 26, 481, 1930.

The  $p_{\rm H}$  of the solutions was reduced in stages by the addition of sulphuric acid, duplicate deposits being prepared at each stage, except in cases where increasing acidity during deposition rendered the preparation of exact duplicates impossible.

On removal from the bath the deposits were washed, dried, weighed, and then lightly polished, and tested for hardness by the Brinell method

using a 1 mm. ball and 10 kg. load.

For examination of the microstructure the deposits were afterwards thickly coated with electrodeposited copper and cut transversely near the centre, the sections thus obtained being ground and polished.

# Control of Acidity.

Frequent determinations of the solution  $p_{\rm H}$  were made in all experiments by the colorimetric method using buffer standards, the accuracy of which had been checked. The results obtained were subsequently corrected to allow for the salt error, the required correction having been separately determined for each solution over the whole  $p_{\rm H}$  range in which it was operated by quinhydrone electrode measurements. The corrected values are given throughout the report. In all the solutions studied, the colorimetric method was found to give a result approximately 0.5  $p_{\rm H}$  units higher than the quinhydrone electrode value in the range  $p_{\rm H}$  3.0 upwards.

In the case of solutions NSB. KC and NSB. C the  $p_{\rm H}$  tended to rise during deposition and the acidity could be kept constant to within close limits by the addition of sulphuric acid as required. In the case of solutions NSB. K and NSB, however, the solution  $p_{\rm H}$  tended to fall owing to low anode efficiency due to the absence of chloride. This was especially marked in the  $p_{\rm H}$  range in which the solutions were poorly buffered, viz,  $p_{\rm H}$  5·5 - 3·5 approximately, and in the case of deposits prepared within this range, the acidity of the solution varied appreciably between the commencement and finish of the run.

In these cases an arbitrary  $p_{\rm H}$  value was taken for the purposes of plotting the curves, which assumed the effective  $p_{\rm H}$  to lie at a point two-thirds of the way downwards from the commencing to the finishing values. The shape of the curves subsequently obtained justified this assumption.

The conditions of deposition are summarised as follows:—

Temperature of the solutions .  $35^{\circ} \pm \frac{1}{2}^{\circ} C$ . Cathode Current Density . . . II Amps./sq. ft. (I-2 Amps./sq. dm.). Duration of Deposition . . . 24 hours.

(equivalent to a thickness of deposit of approximately 0.014 inches (0.35 mm.)).

#### Buffer Characteristics of Solutions.

The buffering properties of each solution were determined over the range of  $p_{\rm H}$  investigated by titrating 2 litre samples prepared as described above with 2N . H<sub>2</sub>SO<sub>4</sub>. Typical curves are shown in Fig. 1.

# Experimental Results.

# Visual Examination of Deposits.

The results of cathode efficiency determinations are shown graphically in Figs. 2 and 3; the deposits from each solution were arranged in order of decreasing  $p_{\rm H}$  and their appearance as regards pitting, and brightness was then summarised and is recorded diagrammatically in the panels in Figs. 2 and 3, the same  $p_{\rm H}$  scale applying to both the curves and the panels.

(1) Summary of Observations relating to the Occurrence of Pitting. —Pitting occurred to some extent in all the solutions investigated with the possible exception of NS.K. Pitting was not observed in the lustrous mirror-bright deposits, nor in general on deposits produced at a  $p_{\rm H}$  lower than 3°0 except in the case of solution NS.C in which pitting occurred at  $p_{\rm H}$  values as low as 2°6. In two solutions, NSB, NSB.K, minute pits barely visible to the naked eye were formed below  $p_{\rm H}$  3°0, and from  $p_{\rm H}$  2°5 downwards there was a tendency for vertical streaks to

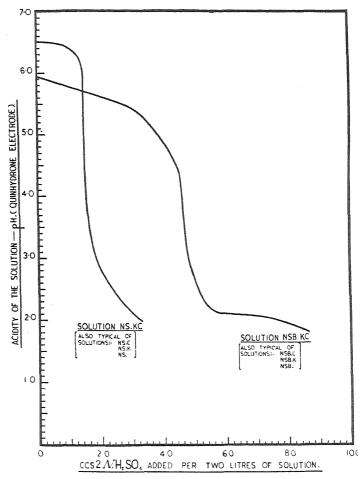


Fig. 1.—Buffer characteristics of the solutions used.

emanate from these minute pits. This type of streak, frequently referred to as a "gas-streak" has previously been described.

The eight solutions may be conveniently divided into three groups according to the intensity of pitting. Thus deposits from solutions NSB, NSB.C, NS.C were severely pitted. None of these solutions contain potassium, whilst two contain chloride. Deposits from solutions NSB.KC and NS.KC, each of which contain both potassium and chloride, were slightly pitted. Deposits from solutions NSB.K, NS.K and NS which do not contain chloride were slightly or not pitted.

Pitting in each solution commenced and ceased, in general, at welldefined acidities and attained a maximum intensity at an intermediate  $p_{\rm H}$ . In one case, viz., NS, there appeared to be two unconnected ranges of acidity in which pitting occurred.

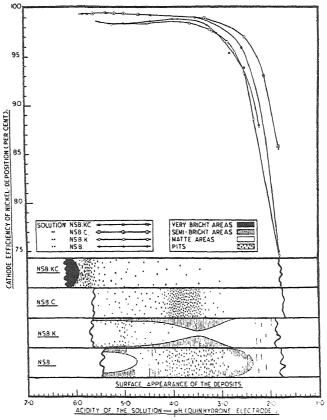


Fig. 2.—Cathode efficiency /  $p_H$  curves and effect of solution  $p_H$  on pitting and appearance of deposits. Buffered solutions (containing boric acid).

The  $p_{\mathbf{H}}$  ranges in which pitting occurred in the various solutions are summarised in Table III.

TABLE III.—Occurrence of Pitting in Relation to Solution  $p_{\rm H}$ .

Solution.	p Range in which Pitting Occurred.	$p_{\mathrm{H}}$ at which Maximum Intensity of Pitting was Observed.
NSB NSB.C NS.C	4·7 - 2·5 5·6 - 3·0 6·3 - 3·0	3:3 4:0 Severely (i) 6:3 pitted (ii) 3:3
NSB.KC NS.KC	5·9 - 3·0 5·8 - 3·5	5.75 \ Slightly 5.8 - 4.5 \ pitted
NS	(i) 6·o (ii) 3·5	Very slightly or not pitted
NS.K NSB.K	3.0 - 3.5 5.65 - 4.3	— J or not pitted

Although pitting was not observed in mirror-bright deposits, it was found that a slight change in the conditions of deposition which caused an alteration in appearance from bright to matt also frequently resulted in the production of pitting. Thus, a slight downward displacement of  $p_{\rm H}$  in solution NSB . KC in the neighbourhood of  $p_{\rm H}$  5.9 effected a change from a semi-bright unpitted, to a matt and severely pitted deposit; occasionally both matt and bright areas were obtained on a single deposit owing to irregular current distribution, and in such cases pitting was generally concentrated in the matt areas immediately adjacent to the bright zones.

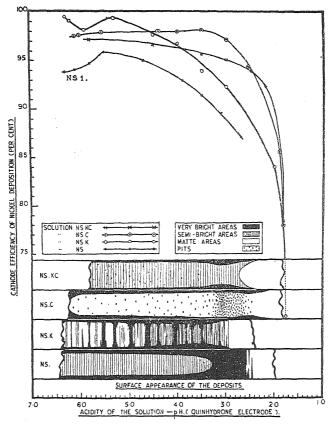


Fig. 3.—Cathode efficiency /  $p_H$  curves and effect of solution  $p_H$  on pitting and appearance of deposits. Unbuffered solutions.

(2) Summary of Observations relating to Surface Brightness of Deposits.—In general, the deposits from the buffered solutions containing boric acid were matt and crystalline whilst those from the unbuffered solutions tended to be lustrous or mirror bright.

Bright deposits were, however, obtained in certain conditions from the buffered solutions; thus in the presence of chloride, the deposits were bright only in a very restricted range towards the upper  $p_{\rm H}$  limit, but in the absence of chloride there was a tendency for brightness to occur at  $p_{\rm H}$  values intermediate between the highest and lowest  $p_{\rm H}$  values studied. This effect was especially pronounced in solution NSB. At all other  $p_{\rm H}$  values investigated matt deposits were produced in the buffered solutions.

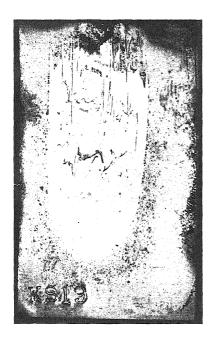


FIG. 4.—Markings suggesting the presence of a partially ruptured film at the cathode surface during deposition. (Solution NS . K,  $p_{\rm H}$  3.5.) (× 2)

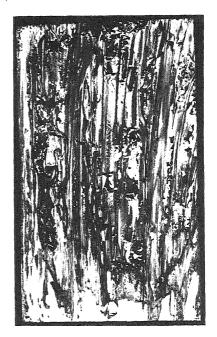
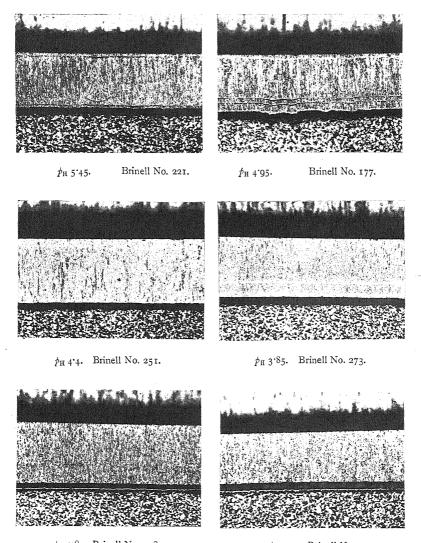


Fig. 5.—Exfoliated deposit prepared in solution NS. K,  $p_{\rm H}$  3'3 (cf. Fig. 4). The deposit prepared under similar conditions at  $p_{\rm H}$  3'0 was sound and matt. ( $\times$  2)

[To face page 736.



 $p_{\rm H}$  2.8. Brinell No. 218.  $p_{\rm H}$  2.2. Brinell No. 174. Fig. g.—Influence of solution  $p_{\rm H}$  on the microstructure of the deposits (× 55). (Solution NSB.) [See page 740.

Deposits from the unbuffered solutions were in general lustrous or mirror-bright and frequently streaky. Solution NSC was an exception, the majority of deposits from this solution being matt. As in the buffered solutions a tendency was observed for maximum brightness in the chloride-free solutions to occur at an intermediate point in the  $p_{\rm H}$  range. Thus it was found that there was a greater tendency for bright deposits to be produced in solutions free from chloride than in corresponding solutions in which chloride was present, this being true of both the buffered and unbuffered groups of solution. In all the solutions, sound matt deposits were obtained at the lowest  $p_{\rm H}$  values investigated. Thus in solution NS. K. at  $p_{\rm H}$  4.0, the deposits were almost entirely bright. At  $p_{\rm H}$ 3.5 mirror-bright markings resembling the pattern of watered silk appeared on the deposit, suggesting the presence of a partially ruptured film at the cathode surface during deposition (see Fig. 4), and at a slightly lower  $p_{\rm H}$  the deposits became seriously exfoliated (see Fig. 5). A marked change took place at about  $p_{\rm H}$  3.0 when the deposits became sound and matt with only an occasional bright streak. Below this  $p_{\rm H}$ , matt deposits were obtained to the end of the series.

#### Cathode Efficiency Results.

1. Buffered Solutions containing Boric Acid.—The cathode efficiency/ $p_{\rm H}$  curves shown in Fig. 2 are of the same general form for all the solutions studied; the cathode efficiency remained approximately constant with change of acidity until  $p_{\rm H}$  3.5 was reached, when it commenced to fall at a rate which increased rapidly with further decrease in  $p_{\rm H}$ .

In the case of both of the solutions free from chloride (viz., solutions NSB and

NSB . K), the cathode efficiency curves lie below those relating to the solutions containing chloride, the presence of Cl' apparently favouring an increase in the cathode efficiency.

Comparison of the curves obtained for solutions NSB. KC and NSB. C suggests that the presence of alkali metal favours a more rapid decline in the cathode efficiency below  $p_{\rm H}$  3.5.

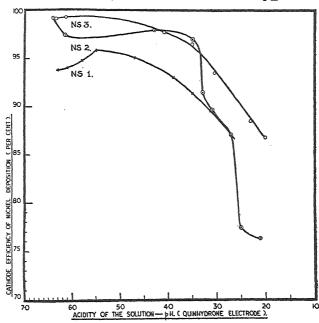


Fig. 6.—Different cathode efficiency  $/p_{\rm H}$  curves obtained with three similar nickel sulphate solutions (NS).

Thus increase in cathode efficiency may result either from (a) the presence of chloride, or (b) the absence of potassium in solutions of the type at present under discussion.

The results of cathode efficiency measurements made in conjunction

With this exception deposits of high hardness were produced in all cases from the solutions at the highest  $p_{\rm H}$  values used, and in every case, the hardness diminished rapidly with decrease in  $p_{\rm H}$  until a critical  $p_{\rm H}$ value was reached at which the abrupt fall in hardness with further lowering of  $p_{\rm H}$  ceased. Below this point, the hardness/ $p_{\rm H}$  relationship was found to differ in the various solutions with the presence or absence of chloride and to a lesser extent of potassium ions. In the case of the two solutions containing chloride ions (NSB. KC and NSB. C), reduction in  $p_{\rm H}$  below the critical point produced relatively little change in hardness; although in these two solutions the hardness was similar above the critical point, the deposits obtained from the solution containing potassium (NSB.KC) were appreciably and consistently harder below the critical point than those produced from the solution free from potassium (NSB.C). The hardness figures obtained from the solutions free from the chloride ion (NSB. K and NSB) showed a marked rise in hardness with decrease in  $p_{\rm H}$  below the critical point up to a well-defined maximum, after which further decrease in  $p_{\rm H}$  resulted in a diminution in hardness, the deposits from the NSB solution becoming progressively softer, whilst those from the NSB. K solution, after an initial fall, rose in hardness to a second but lower maximum and then became progressively softer; the solution containing potassium (NSB. K) in this case yielded somewhat softer deposits than were obtained in the absence of this ion (NSB solution).

Visual examination of the deposits showed that variation in solution  $p_{\rm H}$  produced the same general change in the characteristics of the deposits as was observed in the thin deposits, the appearance of which has been described above. The change in appearance of the deposits with alteration in  $p_{\rm H}$  was in close agreement with what would be expected from the results of the hardness measurements, i.e., the harder deposits tended to be of a lustrous and the softer deposits of a matt appearance. Micro-examination showed that in all cases, the grain size of the hard and lustrous deposits was small but that as the hardness diminished and the deposits became more matt in texture, the grain size increased. This correlation between grain size, surface smoothness and hardness is con-

firmatory of previously published results.

Photographs showing the microstructure of the deposits obtained in NSB solution are given in Fig. 9.

#### PART II. DISCUSSION OF RESULTS.

# 1. Hardness of Electrodeposited Nickel.

In the discussion of the results of a previous investigation 2 in which solutions containing both potassium and chloride ions were employed, it was considered that, whereas the rapid rise in hardness with increase in  $p_{\rm H}$  above the critical  $p_{\rm H}$  could be best explained as due to an effect of basic material formed at the cathode face in modifying the size of the crystals, below this critical  $p_H$  the slight rise in hardness which was found to occur with decrease in  $p_{\rm H}$  might be considered to be due to a direct effect of the increasing amount of hydrogen which is simultaneously discharged with the metal, although this was considered unlikely.

In the present investigation the additional data obtained with respect to the variation of hardness and cathode efficiency with  $p_{\rm H}$  throws considerable doubt on the possible relationship between the amount of hydrogen discharged and the properties of the deposit.

Thus, comparison of the hardness figures obtained from the NSB. KC and the NSB. C solutions shows that the absence of potassium results in the production of appreciably softer deposits below the critical  $\rho_{\rm H}$ ,

whereas although the amount of hydrogen discharged is less in the solution giving the softer deposits, this difference is relatively slight.

n the case of the solutions from which chloride is absent, the disparity between the hydrogen discharged and the hardness of the deposit becomes even more marked. Thus in solutions NSB. K and NSB decrease in  $p_{\rm H}$  below the critical value results in a substantial increase in hardness to a maximum followed by a decrease (see Fig. 8). No corresponding change in the amount of hydrogen discharged occurs, however.

It would thus appear that it is not possible to relate the properties of the deposit to the amount of hydrogen discharged, and in view of the pronounced effect on the characteristics of nickel deposits produced by the precipitation of basic hydroxides in the film of liquid adjacent to the cathode when the solution  $p_{\mathbf{H}}$  is high, it becomes of importance to consider the degree to which this factor also operates to increase hardness when the solution  $p_{\mathbf{H}}$  is low.

# The Formation of Basic Material at the Cathode.

The electrochemical discharge of nickel ions at the cathode is always accompanied by the discharge of hydrogen ions. As there is no evidence that any other electrode process takes place at the cathode, the deviation of the efficiency of nickel deposition from 100 per cent. is therefore the measure of the extent of hydrogen discharge. This removal of hydrogen ions from the liquid adjacent to the cathode in relatively stagnant solutions decreases the acidity compared with that of the bulk of the solution and in consequence a gradient of decreasing acidity is formed from the adjacent solution to the cathode face.

In order to understand fully the reactions which occur at the cathode whereby basic material is formed, it would be necessary to know precisely the composition and  $p_{\rm H}$  of the film of liquid at the cathode face. There is no known method whereby this information may be obtained. It has, however, been established by the results of this investigation together with those of the supplementary investigation on the effect of annealing on the deposits \* that basic material is present in deposits formed in the various solutions over the whole range of  $p_{\rm H}$  studied. It may therefore be concluded that the film of liquid immediately adjacent to the cathode must at least reach the precipitation  $p_{\rm H}$  of the basic salt.

Assuming that it does not exceed this  $p_{\rm H}$ , then the film of liquid adjacent to the cathode is at a constant  $p_{\rm H}$  no matter what is the  $p_{\rm H}$  of the bulk of the solution. This is likely since any tendency to rise in  $p_{\rm H}$  would be checked by further precipitation. If this is the case then the change of efficiency which is found to occur at different  $p_{\rm H}$  values of the solution would appear to be related to changes in the amount of hydrogen discharge which is required to bring the liquid continuously arriving at the cathode face to the precipitation point. It is, however, also necessary to explain the various amounts of basic material which are co-deposited at different acidities as revealed by the differences in hardness of the deposits and by micro-examination of the deposits after annealing in vacuo as shown in the supplementary investigation.\*

It is only possible to conjecture as to the manner in which this may take place. Thus (I) the film of liquid at the cathode face may not be

<sup>\*</sup> See following paper, p. 755.

maintained continuously at the precipitation  $p_{\rm H}$  but may fluctuate between this and a lower value. In this case the amount of basic material would vary with changes in the proportion of the time during which the solution was at the precipitation  $p_{\rm H}$ . This explanation involves periodic phenomena at the cathode face such as has been considered likely to occur on other grounds by various investigators; (2) the film of liquid may be continuously maintained at the precipitation  $p_{\rm H}$  but the thickness of the film may vary. In this case the thicker the film of liquid at the precipitation  $p_{\rm H}$  the greater the amount of basic material that savailable for co-deposition with the nickel and the greater the hardness of the deposit.

Whatever view is finally established as correct the following question then arises: why should there be a rise in hardness as the  $p_{\rm H}$  is decreased below the critical  $p_{\rm H}$  in the case of deposits from all solutions and especially in the solution free from chloride ions in which this rise is very great?

Some indication of the relative amounts of basic material likely to be present at the cathode face during deposition from similar solutions at different acidities may be obtained in the following manner. From the efficiency of hydrogen ion discharge in each case, the weight of hydrogen discharged by unit current in unit time is calculated and from this the equivalent volume of standard acid is deduced. The volume of standard acid necessary to change the  $p_{\rm H}$  of I c.c. of the solution from the precipitation point of nickel hydroxide to the acidity under consideration may be read off from the buffering curve (Fig. I). The removal of a mass of hydrogen ions equivalent to this volume of standard acid from I c.c. of the solution would reduce it to the precipitation point. Hence by proportion the volume of solution brought to the precipitation point by the removal of the calculated amount of acid can be found.

The results of calculations made in this manner, for two typical solutions are shown graphically in Fig. 10. As calculated it appears that in both solutions, above a certain  $p_{\rm H}$  (e.g. NSB. C solution  $p_{\rm H}$  5.3, NSB solution  $p_{\rm H}$  4.0) there is a rise in the amount of basic material, while below this  $p_{\mathbf{H}}$  there is first of all a slow and then finally a rapid rise. Fair agreement between the relative amount of basic material formed and the hardness of the deposit occurs above the critical  $p_{\rm H}$ . lower  $p_{\rm H}$  values, however, the rapid rise in the amount of basic material occurs at a  $p_{\rm H}$  value considerably lower than the rise in hardness of deposits from NSB solution to which it might be expected to correspond. There is, however, an assumption made which is likely to affect the actual shapes of the curves. The calculations are based upon the experimentally determined values for the buffering properties of the bulk of the solution whereas it is really the buffer properties of the cathode film which are involved. There is reason to believe that the solution adjacent to the cathode face is much more dilute than the bulk liquid owing to discharge of nickel ions and the repulsion of anions from the cathode face (this is discussed later). The repulsion will be greatest on the trivalent borate ions so that the composition of the liquid adjacent to the cathode face will, in the case of both of the solutions under discussion, approach that of a dilute solution of nickel sulphate (with and without the presence of chloride ions in the two cases respectively). When the results of calculations for such a solution (e.g. NS. K) are plotted the curve takes the form shown dotted in Fig. 10.

If, now, the variation in the calculated amounts of basic material which tends to form with changes in  $p_H$  of the bulk solution is compared

with the changes in hardness with  $p_{\rm H}$ , it is seen that there is a fair correspondence in the case of the NSB solution except that as the  $p_{\rm H}$ is lowered below 3.0 there is a progressive drop in hardness. divergence may be explicable, in view of the changed conditions at lower  $p_{\rm H}$  values. Thus as the  $p_{\rm H}$  of the bulk solution is decreased below  $p_{\rm H}$  3.0, the solution at the cathode face becomes subjected to increased agitation by rising hydrogen bubbles owing to the greater amount of hydrogen which is discharged. In consequence there may be a decreasing

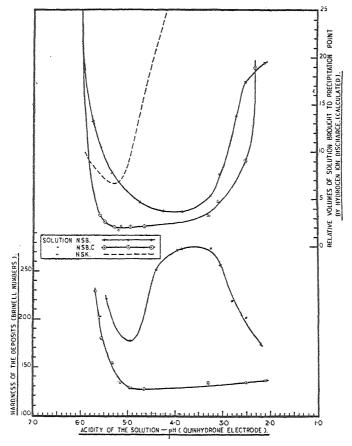


Fig. 10.—Comparison between change in hardness of nickel deposits (lower curves) and the possible variation in amount of basic material produced at the cathode surface (upper curves) with alteration in solution  $p_H$ .

tendency of the solution at the cathode face to rise in  $p_{\rm H}$  to the precipitation  $p_{\rm H}$  since the effect of the hydrogen discharge will be distributed over a greater quantity of solution. It would thus appear that in the NSB solution there are grounds for concluding that the variation in the tendency for basic material to form with change in  $p_{\rm H}$  of the bulk solution is similar to the variation in hardness. On the other hand in the  $p_{\rm H}$  range below the critical  $p_{\rm H}$  there is not the same degree of relationship in the case of the NSB. C solution which differs from the NSB solution in containing chloride ions.

# Significance of Basic Material in Relation to Hardness.

(a) Amount of Basic Material.—The fact that the calculations referred to above indicate that there is a similar rise in the amount of basic material produced at the cathode face in the  $p_{\rm H}$  range below the critical  $p_{\rm H}$  irrespective of the presence of chloride in the solution, whereas there is a striking difference in the effect of  $p_{\rm H}$  on the hardness, might appear to raise doubts as to any direct relationship between hardness and the amount of basic material. The difference cannot be explained as due to difference in the effects of agitation of the solution at the cathode surface in this range of  $p_{\rm H}$  since the cathode efficiencies are similar.

Similarly, the omission of the potassium ion from the NSB. KC solution does not affect the calculated amount of basic material produced over a considerable  $p_{\rm H}$  range (viz.,  $p_{\rm H}$  5·5 — 3·5) although it produces a marked difference in hardness of deposits formed in this  $p_{\rm H}$  range.

Although it would thus appear that the differences in hardness observed cannot be directly related to the amount of basic material produced, this possibility cannot be entirely disregarded in view of the difficulty at present of making proper allowance for all the factors concerned, as for example the effect of the chloride and potassium ions on the buffer characteristics of the cathode film.

There are, however, reasons for concluding that these constituents are likely to have an important effect on the nature of the basic material which would appear to afford an adequate explanation of the experimental results.

(b) Nature of Basic Material.—The effect on the characteristics of the deposit produced by basic material precipitated in the film of liquid adjacent to the cathode is likely to vary considerably according to whether the material is present in the colloidal or in the flocculated condition.

The pronounced effect of colloidal matter on the structure and properties of electrodeposits is well known. In the case of a positively charged sol such as nickel hydroxide sol for example, the material is attracted towards the cathode face where it becomes discharged together with the nickel ions. The inclusion of hydroxide, or more probably oxide (as there will be a pronounced tendency for the combined water to be removed into the solution at the moment of discharge) in the deposit in this way interferes with the normal process of crystal formation and results in a small grain size and an increased hardness.

A neutral precipitate in the neighbourhood of the cathode, however, is not likely to have any appreciable direct influence on the structure of the deposit, especially if it becomes dispersed in the solution (as is likely, due to convection and agitation effects, in the neighbourhood of the cathode) when in normal conditions it would be rapidly dissolved. An indirect effect, may, however, be produced by such a precipitate and this will be discussed later.

Experiments have shown that if nickel hydroxide sol is added to any of the solutions under consideration immediate precipitation occurs provided the solution is sufficiently high in  $p_{\rm H}$  not to redissolve the hydroxide; the precipitation is due to rapid discharge of the positively charged sol by the negatively charged anions which are present in high concentration. From investigations on nickel hydroxide sols 5 it may be

<sup>&</sup>lt;sup>5</sup> "On the Preparation of Colloidal Solutions of Nickel and Cobalt Hydroxides and some other compounds of these Metals," O. F. Tower, and M. C. Cooke, *J. Physic.*, Chem., 26, 728, 1922.

concluded that if anions are present in even moderate concentration right up to the cathode face, any basic material formed is likely to be in the condition of a neutral precipitate.

# The Influence of Potassium and Chloride Ions on the Amount and Nature of the Basic Material.

In the electrolysis of nickel depositing solutions of the type studied in this investigation, it is unlikely that conditions exist which entirely preclude the formation of nickel hydroxide sol. Thus during electrolysis there is a general repulsion of the negative anions in the solution by the negatively charged cathode and attraction of these anions towards the positively charged anode. The migration rate is slow and the drift of anions is opposed by diffusion, agitation and convection together with the tendency of such cations as are approaching the cathode to drag along with them an atmosphere of negative anions. There will thus always be likely to be a certain concentration of anions in the liquid relatively close to the cathode face. The concentration will. however, fall off as the cathode face is actually approached since the force of electrostatic repulsion will become very large as the distance is decreased to a small value. It is thus likely that in the thin film of liquid immediately adjacent to the cathode face the concentration of anions will drop to zero. As the discharge of hydrogen which results in the solution rising in  $p_H$  towards the precipitation point \* occurs at the cathode, it will be in the inner layer of liquid close to the cathode face that the precipitation point will be reached. It is thus likely that here nickel hydroxide will form in colloidal condition and being positively charged will be attracted to the cathode where it will tend to interfere with crystal growth, i.e., will influence the hardness and properties of the deposit. If, however, the amount of solution which is brought to the precipitation  $p_{\rm H}$  extends beyond the inner layer, which alone is free from anions, then flocculation of the sol is likely to occur in the outer layers with the production of an uncharged precipitate (probably a basic precipitate of nickel hydroxide + anion). Owing to its electrically neutral character this precipitate will not be electrically attracted to the cathode face and is thus less likely to exert a direct effect on the properties of the deposit.

It would thus appear that any factors which tend to diminish the thickness of the liquid layer in which colloidal nickel hydroxide can be formed will tend to diminish interference of the growth of crystals by the presence of colloidal matter, i.e., will tend to encourage the formation of larger crystals and softer deposits. It might be expected that this effect is likely to arise from the presence of chloride ions in the solution. These ions are smaller than the sulphate ions and as they have the same kinetic energy their diffusibility is greater. Also they carry only one negative charge while the sulphate ions carry two. There will thus be less tendency for the chloride ions to migrate away from the cathode zone during the passage of current. More important still, they will be able to approach closer to the cathode face than the sulphate ions. Thus it would appear that the zone sufficiently free from anions to allow

<sup>\*</sup> The term "precipitation point" is used to indicate the minimum  $p_{\tt H}$  value at which nickel hydroxide can be present in either a colloidal or a flocculated condition.

the precipitated basic material to be retained in the sol form, will be decreased when chloride ions are present in the solution.

The effect of chloride ions would thus tend to encourage the formation of softer deposits as has been found in the low  $p_{\mathbf{H}}$  range under consideration.

If the effect of the presence of chloride ions is as described above then the hardening effect of potassium ions in solutions also containing chloride ions might be anticipated owing to the known stabilising action of potassium on positively charged colloid sols. Thus it has been found in a number of investigations that a greater concentration of anions is required to cause the flocculation of an inorganic sol when there is also present in considerable concentration cations likely to stabilise the sol. It was concluded by Tower 5, 6 for example, that potassium ions tend to stabilise the nickel hydroxide sol. In consequence, if potassium ions are present in the liquid adjacent to the cathode face a greater thickness of liquid may reach the precipitation  $p_{\rm H}$  with the resulting formation of sol, before the zone is reached in which the concentration of chloride ions is sufficiently high to more than counter-balance the stabilising effect of the potassium ions. This implies that of the basic material which is formed a greater proportion will tend to remain in the sol form if potassium ions are present and in consequence the deposit will tend to be harder. That potassium ions will concentrate in the liquid film adjacent to the cathode face is inevitable since the positively charged potassium ions are not only highly diffusible but are electrostatically attracted to the cathode, and as they are not discharged they will tend to reach a relatively high concentration. This would explain the difference observed in the  $p_{\rm H}$  range below the critical  $p_{\rm H}$  between solution NSB. KC containing potassium ions and the NSB. C solution not containing potassium ions.

It has been found, however, that in the absence of chloride ions, the presence of potassium, in the range of  $p_{\rm H}$  under consideration, causes a softening of the deposit which might appear to throw doubt on the

explanation suggested above.

There is, however, experimental evidence to show that the flocculated precipitate may have a pronounced indirect effect upon the hardness of the deposit by influencing the relative rates of arrival of nickel and hydrogen ions to the cathode face, and that it is due to the modifying influence of the potassium ions on this indirect effect that the contradictory effect of potassium in non-chloride solutions is explained.

# The Indirect Effect of Flocculated Basic Material on the Conditions at the Cathode Face.

Flocculated basic material, if present in a loose form in which it is easily dispersed and dissolved in the bulk of the solution, is not likely to exert any appreciable effect on the structure of the deposit or on the cathode efficiency. If, however, the material is precipitated in a condition such that it is not readily dispersed, it may have a pronounced indirect effect on the characteristics on the deposit. For example, it may be precipitated in the form of a membrane which is selectively permeable to nickel and hydrogen ions, allowing the smaller and more

<sup>6&</sup>quot; Note on Colloidal Nickel Hydroxide," O. F. Tower, J. Physic. Chem., 28, 176, 1924.

mobile hydrogen ion to pass in preference to the nickel ion. Under these conditions there will be an increase in the rate of discharge of hydrogen, *i.e.*, a fall in cathode efficiency. As a consequence of this, the average  $p_{\rm H}$  of the film of liquid between the membranous precipitate and the cathode will rise so that there will be a greater tendency for the formation of basic material. As this increased amount of basic material is produced in the film of liquid relatively free from flocculating anions there will be more sol produced; the increase in the amount of sol coupled with the decrease in concentration of nickel ions will tend to increase the hardness of the deposit.

The effect described above is likely to vary in degree with the structure and thickness of the film, both of which will be considerably influenced by the buffering properties of the solution and by the presence of stabilising cations such as potassium or flocculating anions such as chloride: the structure of the film will be considerably influenced by a number of complex factors which determine its rate of flocculation. If the structure of film is sufficiently coarse, without being readily dispersible, its selectively permeable properties will be destroyed and the material will then function merely as an obstruction to the free movement of solution in the neighbourhood of the cathode and there will thus be less opportunity for convection and diffusion to effect dispersion of the more alkaline solution adjacent to the cathode. This will tend to reduce the hydrogen ion concentration of this liquid and increase the concentration of sol thus giving rise to a higher cathode efficiency and an increased hardness, although the effects produced in this way might be expected to be much less pronounced than in the case of the selectively permeable membrane.

The production of a dense membrane such as would be selectively permeable to different ions is more likely to occur in relatively unbuffered solutions where even a small hydrogen discharge will cause a rapid rise in  $p_{\rm H}$  of the liquid adjacent to the cathode.

Definite evidence of the production of such a precipitate was observed during the formation of deposits in some of the solutions free from boric acid. Thus in the nickel sulphate solution (NS) in a certain range of  $p_{\rm H}$ , sheath-like films were formed which became detached from the cathode and were then clearly visible. A similar effect but to a slighter degree was observed in the nickel sulphate solution containing potassium sulphate (NS.K). Indirect evidence of the presence of such films was obtained in the results of cathode efficiency measurements in the unbuffered solutions (cf. p 738). Reference to Fig. 3 shows that the cathode efficiency in a nickel sulphate solution NS is lower over the whole range of  $p_{\rm H}$  tested than in the NSB. KC solution. Yet it would appear that in the more highly buffered solution, the hydrogen ion concentration of the film of liquid adjacent to the cathode should be higher than in a poorly buffered solution and that the cathode efficiency should in consequence be less. That this is the case in certain circumstances can be shown by the lowering in cathode efficiency produced by a considerable increase in the buffering properties of the NSB, KC solution by the addition of 50 g. per litre of sodium acetate. The explanation of this anomaly is obtained if the film of precipitate is acting as a selectively permeable membrane in the manner already discussed.

On the addition of potassium sulphate to the nickel sulphate solution, the cathode efficiency over the whole range of  $p_H$  is increased. It is still not so high, however, in the lower  $p_H$  ranges as in the better buffered

NSB. K solution. On the reasoning given above, there is still some restriction to the approach of nickel ions to the cathode face, but the effect is less than in the nickel sulphate solution owing to the stabilising action of the potassium ions in reducing the amount of basic material precipitated.

The introduction of chloride into the unbuffered solutions exerts a marked effect on the cathode efficiency and on the formation of an obstructive membrane. Thus reference to Fig. 3 shows that the cathode efficiency is higher over a wide range of  $p_{\rm H}$  in solutions NS . C and NS . KC than in corresponding solutions free from chloride. This is consistent with the experimental observation of the difficulty of obtaining visible films from the chloride solutions. It was in fact found necessary to raise solution NS . C to an abnormally high  $p_{\rm H}$  in order to get any visible evidence of film formation whereas, as indicated above, films were seen in solution NS over a wide range of  $p_{\rm H}$ . This difference would appear to be due to the effect of chloride ions on the physical condition of the flocculated basic material in rendering it more easily dispersed and dissolved in the bulk of the solution and so minimising the tendency to film formation.

In the case of the buffered solutions the  $p_{\rm H}$  of the solution near the cathode is likely to be somewhat lower owing to the better buffering properties of the solution and there will not in consequence be as great a tendency for the production of a dense film. At the same time, over the whole  $p_{\rm H}$  range, the cathode efficiency in solutions free from Cl' is lower than in similar solutions containing Cl'; this is consistent with the existence of a film in solutions free from chloride which is to some extent selectively permeable and which would therefore operate to reduce cathode efficiency and increase hardness in the manner already described. In these solutions, the presence of potassium, by its stabilising action on the sol will somewhat reduce the effectiveness of the film as a selectively permeable membrane and its action in this respect would appear, from the fact that it results in a somewhat lower hardness, to more than counterbalance the effect of the increased amount of sol.

It is necessary, however, to emphasise that these marked differences between the two types of solution may be modified both at higher and at lower  $p_{\rm H}$  numbers than the range under consideration. As the  $p_{\rm H}$  is lowered there will be an increasing tendency for the precipitate produced in the non-chloride solution to be dissolved so that marked differences in the rates of solubility of the precipitated material will tend to disappear. This is consistent with the fact that at low  $p_{\rm H}$ , the hardness of deposits from both types of solution tends to approximate to a similar low value.

At higher  $p_{\rm H}$  than the range under consideration the fact that the hardness is less influenced by the presence of chloride ions may be due to the fact that the  $p_{\rm H}$  of the liquid adjacent to the cathode face is reaching a value at which the solubility of the basic chloride is diminished. This effect may explain why in practically all the solutions the hardness curves tend to approximate to similar values above the critical  $p_{\rm H}$ . In these circumstances the solutions containing chloride ions will tend to produce a greater amount of obstructive material at the cathode face, which, by its indirect action in causing the  $p_{\rm H}$  of the cathode film to rise in the manner previously discussed, will have a hardening effect on the deposits; this may more than counterbalance the softening effect ordinarily attributable to the chloride ion.

### 2. Pitting.

Examination of the deposits obtained in the course of this investigation, the results of which are indicated pictorially in Figs. 2 and 3, shows that pitting occurs in the case of most of the solutions in certain ranges of  $p_{\rm H}$ . In view of the fact that care was taken by suitable preparation of the cathodes to exclude the possibility of basis metal pitting, and that materials of high purity were employed, it would appear that solution pitting does not necessarily result from the presence of impurities, as was previously suggested.1

Of the solutions which have been examined, only two are of practical importance-viz., NSB. KC and NSB. C. As the occurrence of pitting in solutions of this type has been studied by other investigators, it is of importance to consider these previous observations in relation to the

present results.

# Discussion of Previous Work on the Relation between Pitting and Solution $p_H$ .

Thompson, 7 and later Montillon and Cassel, 8 examined the effect of solution  $p_H$  on the tendency to pitting in a solution very similar to the NSB. KC solution and concluded that pitting was most likely to occur with reduction in  $p_{\rm H}$  below  $p_{\rm H}$  40. This conclusion is contrary to the results found in the present investigation since it was found that pitting was entirely absent in this solution below  $p_{\rm H}$  3.0 while a marked tendency to pitting was observed in high  $p_{\rm H}$  ranges. This discrepancy is probably due either to the confusion between basis metal pitting and solution pitting by previous investigators or to their use of insufficiently pure materials.

Kreuger and Foerster 9 working with a solution similar to NSB.C found that pitting disappeared with reduction in  $p_{\rm H}$  below a certain value. This is in general consistent with the results obtained in the course of the present work although the actual  $p_H$  value below which Kreuger and Foerster found pitting to cease is somewhat higher.

### Hydrogen Discharge in Relation to Pitting.

The facts that pitting is due to the screening effect of hydrogen bubbles and that the amount of hydrogen discharged is increased with decrease in solution  $p_{\rm H}$  are largely responsible for the popular assumption that pitting should be increased with decrease in solution  $p_H$ . Examination of a large number of deposits of different thicknesses formed on cathodes free from surface imperfections and in solutions prepared from highly purified chemicals has shown, however, that the reverse is actually the case, and that pitting may be eliminated by the use of a sufficiently low  $p_{\rm H}$ , whereas it is liable to occur at higher  $p_{\rm H}$  values.

Examination of a magnified image of the cathode during nickel deposition using the apparatus described in the previous report i has shown that in the low  $p_{\rm H}$  range in which the deposits were found to be unpitted. hydrogen bubbles appeared in large numbers over the surface of the

<sup>&</sup>lt;sup>7</sup> "The Acidity of Nickel Depositing Solutions," M. R. Thompson, J. Amer-

Electrochem. Soc., 41, 333, 1922.

8 "Acidity of Cobalt and Nickel Plating Baths," G. H. Montillon and N. S. Cassel, J. Amer. Electrochem. Soc., 45, 259, 1924.

9 "The Behaviour of Nickel Anodes," F. Foerster and F. Kreuger, Z. Elektrochem., 33, 406-425, 1927.

cathode; these, however, in general became quickly detached when only small in size. On the other hand in the higher  $p_H$  range, although fewer bubbles were generally produced, they tended to remain longer in contact with the cathode and to grow to a larger size before becoming detached.

A relatively rapid rate of hydrogen discharge would appear to favour decreased pitting in at least two ways: (a) There is a more rapid growth of hydrogen bubbles relative to the rate of increase in thickness of the deposit. In consequence the depressions formed will be shallower and will be less effective in holding the bubbles in position in the period during which they are growing to the size at which buoyancy finally causes their detachment; (b) The greater amount of agitation set up by the more rapid bubble discharge will tend to produce dislodgement of the bubbles at an earlier stage.

These factors, while possibly accounting in the main for the greater freedom from pitting at low solution  $p_{\rm H}$ , are clearly inadequate to explain all the results obtained from the two solutions of practical importance previously referred to. Thus, very serious pitting was found in deposits produced from the NSB. C solution in the  $p_{\rm H}$  range 4.2 - 3.4, whereas pitting in this p<sub>H</sub> range in the NSB. KC solution was only very slight; yet in this  $p_H$  range the rate of hydrogen discharge, as evidenced by cathode efficiency measurements was found to be identical in the two solutions. Further, with increase of ph above 4.2 in the NSB. C solution, pitting becomes less pronounced, although conditions should favour a slower growth of hydrogen bubbles and less agitation at the cathode face.

It would thus appear that factors other than those directly connected with the rate of hydrogen discharge are operating to affect the degree of bubble adhesion.

# Basic Material in Relation to Pitting.

Foerster and Kreuger 9 suggested that the presence of nickel hydroxide at the cathode face has an important bearing on the degree of pitting in the higher  $p_{\rm H}$  ranges in which they found this defect to be most prevalent, and they quote experiments in which a visible precipitate was observed to coat the bubbles as a membrane and to retard their detachment from the cathode.

Although no visible precipitated matter has been observed surrounding the bubble walls in any of the present experiments with the NSB.C solution (which is similar to that used by Kreuger and Foerster), there would appear to be a number of reasons to account for increased bubble adhesion caused by the presence of basic material formed at the cathode face; and since it has already been shown that the evidence of hardness measurements points to the presence of this material in the solution adjacent to the cathode (either in a colloidal or flocculated condition), it becomes of considerable importance to examine the possible effect of basic material on pitting.

1. Colloidal Basic Material.—Colloidal basic material formed at the cathode during nickel deposition is positively charged and has been considered 10, 11 to increase the adhesion of bubbles to the negatively

<sup>10 &</sup>quot;Mechanically Perfect Electrolytic Nickel," C. P. Madsen, J. Amer.

Electrochem. Soc., 45, 249, 1924.

11 "The Commercial Deposition of Nickel," E. J. Dobbs, J. Electroplaters' and Depositors' Tech. Soc., 2, 1927.

polarised cathode if present in the bubble interface. The reduction in pitting with reduction in  $p_{\rm H}$  in the NSB. KC solution might appear to favour this view, since pronounced pitting occurs under conditions which, as shown by the high hardness of the deposits, favour the presence of a relatively large amount of colloidal matter at the cathode face. With a small reduction in  $p_{\rm H}$ , however, the tendency to pitting becomes only slight, whereas the hardness is still high.

Furthermore, no satisfactory relationship between colloidal material and pitting would appear to be possible in the case of the NSB. C solution. In this solution, the amount of colloidal matter present at the cathode face (as evidenced by the hardness of the deposits), is practically constant over the  $p_{\rm H}$  range 5.0 - 2.0, although marked changes in the tendency to pitting occur in this range. Also the deposits formed in this  $p_{\rm H}$  range from the NSB. C solution are appreciably softer (indicating less colloidal matter) than those from the NSB. KC solution, although

they are considerably more pitted.

2. Flocculated Basic Material.—It is well known that the stability of foams is increased by the presence of finely divided material in the bubble interface, and this fact was probably the basis of Kreuger and Foerster's suggestion that a membrane of precipitated hydroxide was causing the bubbles to adhere to the cathode face. It does not, however, appear to be necessary that the flocculated material should surround the bubble. In the case of a vertically arranged cathode, the maximum stress on the bubble wall tending to cause its detachment will be in the nature of tension on the underside of the bubble at its junction with the cathode face. An accumulation of finely divided precipitate around the base of the bubble will thus tend to prevent its detachment by increasing its rigidity in the region of maximum stress; attraction of this basic material to the cathode by surface forces may also tend to increase the adhesion of the bubble.

It would thus appear that the adhesion of a bubble to the cathode will be increased by the presence of flocculated material around the area of contact of the bubble and the cathode, and that it is therefore unnecessary for the flocculated matter to be present in visible quantity. Since the zone of liquid in which flocculated material is most effective in promoting adhesion of the bubbles is close to the cathode surface, it will tend to remain high in  $p_{\rm H}$  and so prevent solution of the flocculated matter even when the bulk of the liquid is at relatively low  $p_{\rm H}$  (especially as the solution immediately surrounding the bubble will be comparatively stationary and unaffected by the general upward streaming of liquid over the cathode). Furthermore, the quantity of basic material around the base of the bubble, and hence the amount of flocculated matter and the adhesion of the bubble, will tend to be augmented by prolonged contact of the bubble with the cathode owing to the screening from agitation and diffusion; this will tend to result in the solution adjacent to the bubble rising to an abnormally high  $p_{\rm H}$ . It is significant in this connection to observe that traces of precipitated matter are frequently found in pits and on the rim of the lower side of the pit. and that certain pits have black interiors (this is particularly characteristic of those formed in the NSB. C solution in the  $p_{\rm H}$  range 4.2 - 3.4) suggesting that partial reduction of the basic material has taken place.

The experimental evidence, summarised pictorially in Figs. 2 and 3, is in close agreement with the explanation of solution pitting in pure solutions in terms of flocculated basic material at the cathode face.

Thus in the NSB. C solution, pitting occurs in maximum intensity in the  $p_{\rm H}$  range  $4\cdot 2-3\cdot 4$ , which is the range in which an increased amount of basic material would be expected to be formed from the results of hardness tests in the NSB solution (see Fig. 8). The addition of chloride to the NSB solution (converting it into the NSB. C solution) causes flocculation of the colloidal matter, thus converting it into a form which does not effect hardness but which has a marked influence in promoting pitting.

Further evidence of marked pitting when flocculated basic material is likely to be high is shown in the corresponding solutions free from boric acid, viz., NS. C and NS. In solution NS the maximum hardness, as indicated by the degree of brightness of the deposits, occurs in the  $p_{\rm H}$  range  $3\cdot 3-2\cdot 6$ . An increased quantity of basic material is therefore to be expected in this range. Upon the addition of chloride to the solution (converting it into NS. C) there will therefore be a maximum amount of flocculated basic material, and this occurs in the  $p_{\rm H}$  range in which pitting was found to be at a maximum.

Corroboration of the above hypothesis is also obtained on consideration of the effect of alkali metal and alkaline earth metal ions on pitting.

# Effect of Alkali Metal and Magnesium Ions on Pitting.

1. Potassium.—The presence of potassium was found to have a pronounced effect in decreasing the amount of pitting.

This effect is particularly marked in the range  $p_{\rm H}$  4·2 - 3·4 in buffered solutions containing chloride and is also apparent in the range  $p_{\rm H}$  3·2 - 2·6 in the unbuffered solution containing chloride, as shown by comparison of the deposits from the NSB. KC and NSB. C solutions (Fig. 2) and the NS. KC and NS. C solutions (Fig. 3). (See also results shown in Table IV.) This may be explained by the reduction in the amount of flocculated matter due to the stabilising action of the potassium ion in the manner already discussed.

In buffered solutions free from chloride the presence of potassium also results in a decrease in the amount of pitting in the low  $p_{\rm H}$  range by diminishing the quantity of basic material flocculated by the sulphate ions. In the unbuffered solutions free from chloride, the potassium would appear to function in a similar manner although the amount of pitting was only slight in its absence.

The presence of potassium thus results in a striking reduction in the intensity of pitting in a variety of solutions, and this is consistent with its action in stabilising the colloid at the cathode face and thus reducing the degree to which flocculation occurs.

2. Sodium, Lithium, Ammonium and Magnesium.—A study was made of the effect on susceptibility to pitting of the addition of sodium, lithium, ammonium and magnesium chlorides respectively to NSB solution. The results which are given in Table IV. show that the alkali metal ions, sodium and lithium, tend to diminish pitting appreciably, whilst negligible effects are produced by ammonium and magnesium.

These results give additional support to the view that the amount of flocculated matter present at the cathode face exerts an important action in increasing the adhesion of hydrogen bubbles since the effectiveness of potassium, sodium and lithium in stabilising certain inorganic sols against flocculation by chloride and sulphate ions would be expected to be greater than that of magnesium and ammonium.

TABLE IV.—Influence of Alkali Metals and Magnesium Ions on Pitting.

The chloride additions referred to in this table were made to NSB solution, the sulphate additions to NSB. C solution.

Cation Added.	Amount Added (g. per litre).	Prevalence of Pitting.	p <sub>H</sub> Range Examined.	
Nickel, (NiCl <sub>2</sub> 6H <sub>2</sub> O) Potassium, (KCl) Sodium, (NaCl) Lithium, (LiCl)  Ammonium, (NH <sub>4</sub> Cl) Magnesium, (MgCl <sub>2</sub> 6H <sub>2</sub> O)	Equivalent to 19 g./l. potassium chloride.	Severe pitting. Very slight pitting. Very slight pitting. Slight pitting more than with potassium. Severe pitting. Severe pitting.	5.5 — 3.0 5.5 — 3.0 5.5 — 3.0 5.5 — 3.0 5.5 — 3.0	
Potassium sulphate, (K <sub>2</sub> SO <sub>4</sub> )	0.05 g./l. 0.15 g./l. 0.35 g./l. 0.75 g./l.	Severe pitting. Severe pitting. Slight pitting. Very slight pitting.	р <sub>н</sub> 3·6 only. р <sub>н</sub> 3·6 only. р <sub>н</sub> 3·6 only. р <sub>н</sub> 3·6 only.	

# Summary and Conclusions.

The cathode efficiency, surface appearance (particularly as regards pits), and Brinell hardness of nickel deposits prepared at various acidities from a group of solutions each consisting of nickel sulphate together with one or more of the following substances: boric acid, potassium sulphate, potassium chloride, nickel chloride—have been examined; materials of high purity were used for the preparation of the deposits. The results have been summarised graphically and pictorially.

Deposits of high hardness were produced in all cases examined from the solutions at high  $p_{\rm H}$ , and reduction in solution  $p_{\rm H}$  effected a rapid reduction in hardness until a critical value was reached at which the abrupt fall in hardness with further lowering in  $p_{\rm H}$  ceased. Below this point the hardness  $p_{\rm H}$  relationship was found to vary in the different solutions according to the presence or absence of chloride and to a lesser extent of potassium ions. In the solutions containing chloride, reduction in  $p_{\rm H}$  below the critical  $p_{\rm H}$  produced relatively little change in hardness, the solution containing potassium yielding appreciably and consistently harder deposits than that free from potassium. In solutions free from chloride, the deposits showed a marked rise in hardness with decrease in  $p_{\rm H}$  below the critical point up to a well-defined maximum, after which further decrease in  $p_{\rm H}$  resulted in a diminution in hardness; in this case the solution containing potassium yielded somewhat softer deposits than were obtained in the absence of that ion. The results indicate that no direct relationship between hardness and the amount of hydrogen discharged can be established; the suggestion previously advanced that basic material precipitated in the liquid adjacent to the cathode face is responsible for the hardness of nickel deposits is substantiated and elaborated.

By calculation from the buffering properties of the solution and the cathode efficiency it is shown that the depletion of hydrogen ions from the liquid adjacent to the cathode may result in an increasing amount of basic material being present at the cathode face as the  $p_{\rm H}$  is decreased. It is considered that the basic material is initially formed in the colloidal state and is positively charged. In this state it migrates to the cathode and, by inclusion on the crystal faces, restrains crystal growth, causing the formation of a fine grained and hard deposit.

In the presence of negatively charged anions, however, the colloidal material tends to be discharged and flocculated; the resulting neutral precipitate may have no effect on the deposit owing to its being swept into the bulk of the solution and there dissolved, or it may exert an indirect effect by remaining in the proximity of the cathode as an obstructive or even semi-permeable membrane. It is considered probable that chloride ions have a greater flocculating effect than sulphate ions owing to their closer approach to the cathode, whilst the presence of potassium ions will tend to oppose the flocculation.

In the absence of chloride ions there is evidence, from the observation of films upon the cathode and from cathode efficiency figures, that the flocculated precipitate obstructs the free movement of the solution and thus favours the formation of a greater amount of colloidal material; the obstructive nature of the precipitate is diminished in the presence of potassium, and this more than counterbalances the influence produced by

its stabilising effect on the colloidal material.

The manner in which these effects influence the hardness of the deposit

obtained both above and below the critical  $p_{H}$  is discussed.

The intensity and distribution of the defect of pitting observed in the deposits obtained is recorded. It is found in general to be associated with the absence of potassium and the presence of chloride and to be dependent to a marked degree upon the acidity of the solution, being absent in all cases from deposits prepared at  $p_{\rm H}$  values below 2.6 (quinhydrone). It has not been found possible to correlate the occurrence of the defect with the rate of hydrogen discharge from the cathode or with the presence of colloidal material at the cathode face.

The factor which is chiefly responsible for increasing the adhesion of bubbles to the cathode face is considered to be finely divided basic material of neutral electrical properties which is absorbed in the gas-liquid interface close to the cathode.

In agreement with this view it is found that pitting occurs to a maximum degree in each solution in the range of  $p_{\rm H}$  in which the greatest quantity of flocculated matter is likely to be formed. The influence of chloride in stimulating, and potassium ions in inhibiting, the defect is thus clearly associated with the flocculating and stabilising effect respectively of these ions upon the basic material present; the similar but lesser inhibiting effect of sodium and lithium is in agreement with this view.

The authors desire to extend their thanks to Mr. A. W. Hothersall, M.Sc., for assistance in the preparation of the paper.

# THE EFFECT OF ANNEALING ON THE MICRO-STRUCTURE AND MECHANICAL PROPERTIES OF ELECTRODEPOSITED NICKEL.

By G. E. GARDAM AND D. J. MACNAUGHTAN.

Received 15th May, 1933.

The following is an account of the fourth part of a general investigation into the causes and prevention of pitting in electrodeposited nickel carried out in the Research Department, Woolwich, for the Electrodeposition Research Committee of the Department of Scientific and Industrial Research, and in particular is supplementary to the preceding paper.\*

As a result of various recent investigations, it has been established that the Brinell hardness of electrodeposits of a number of metals may be varied over a wide range by alteration in the conditions of deposition. It has been found, however, that whereas the Brinell hardness of the softest deposits of certain metals such as copper is as low or lower than that of the fully annealed pure metal produced by ordinary metallurgical methods, that of electrodeposited nickel and certain other metals is always higher.

In the case of electrodeposited nickel it was suggested by Macnaughtan and Hammond  $^1$  and substantiated in the preceding paper  $^*$  that an increased hardness can in all cases be correlated with conditions in which a greater amount of colloidal basic material is present in the solution adjacent to the cathode and is due to co-deposition of this colloidal material with the nickel. This view receives support from previous work by O'Sullivan,  $^2$  who concluded that the increase in smoothness and brittleness of nickel deposits which occurs with rise in solution  $p_H$  is due to the presence of increasing amounts of nickel hydroxide in the deposit.

O'Sullivan attempted to prove the actual presence of oxide in the deposit by quantitative analytical methods, but his results were inconclusive. In view of the well-known powerful effect of minute amounts of organic colloids on the structure of deposits in restricting their crystal growth, it would not be surprising if the actual amount of combined oxygen in the form of colloidal basic material which is required to effect considerable modification in structure and properties, was too small to be capable of quantitative estimation; similarly the fact that no direct evidence of the presence of co-deposited material is obtained by micro-examination of the deposits might be anticipated. It appeared likely, however, that if films of basic material were present around the crystals in nickel deposits, an annealing treatment which would cause grain growth of the nickel would cause breakdown of such films, and, as a result of the reduction in boundary surface of the crystals, the material might become concentrated in amounts sufficiently large to be visible under the microscope.

The work described in this investigation consisted therefore in the preparation of nickel deposits under controlled conditions and the examination, both before and after annealing, of their microstructure, Brinell handward and applications and the second of the condition of the

hardness and mechanical properties.

\* Page 720

1" The Influence of Acidity of the Electrolyte on the Structure and Hardness of Electrodeposited Nickel," D. J. Macnaughtan and R. A. F. Hammond, Trans. Faraday Soc., 27, 633, 1931.

Faraday Soc., 27, 633, 1931.

2 "Studies in the Electrodeposition of Nickel. Part I. The Effect of p<sub>H</sub> and of Various Buffering Agents; the Presence of Oxygen in the Deposits," J. B. O'Sullivan, Trans. Faraday Soc., 26, 89, 1930.

# Experimental Methods.

#### Materials Used.

In view of the pronounced effect on the properties of nickel deposits which may be caused by small amounts of impurity derived from the salts or anodes used it was essential to use materials of as high a purity as possible. Particular care was taken to avoid impurities of an organic nature.

- 1. Salts: (a) Nickel Sulphate of good quality was subjected to the permanganate treatment previously described; 3 in the case of the nickel sulphate to be used for solutions free from alkali metals, ammonium persulphate was used in this treatment instead of potassium persulphate.
- (b) Nickel Chloride was also subjected to the permanganate treatment. The other salts used were commercially pure recrystallised chemicals and each was substantially free from organic matter as shown by titration with potassium permanganate of a hot solution acidified with sulphuric acid.
- **2.** Anodes.—The anodes consisted of plates of electrodeposited nickel of which the following is a typical analysis:—

Cobalt			0.07 per cent.
Manganese			0.001 ,,
Copper	•		0.02 ,,
Iron			0.015 ,,
Zinc			0.01 ,,
Lead			Trace.
Silicon			Trace.
Carbon			Nil.

3. Cathodes. — Brass sheets  $8\times 6\times \frac{1}{16}$  inch thick were used as cathodes. Prior to use these sheets were electroplated with copper to a thickness of approximately 0.001 inch to prevent basis metal defects affecting the deposit. A film of copper sulphide was then formed upon the sheet by immersion in a 5 per cent. solution of sodium sulphide to facilitate separation of the nickel deposit from the basis metal and this in turn was coated with a deposit of copper (0.0005 to 0.001 inch thick) before introduction of the cathode into the nickel depositing bath.

#### Composition of Solutions.

For convenience of reference, the solutions have been designated by groups of letters representing their constituent ions. Thus N represents

TARLE	T	.—Composition	OF	SOLUTIONS	TISED

Key Reference. Letters of Solution. Nickel Sulphate, NiSO <sub>4</sub> 7H <sub>2</sub> O, g. Per Litre.		Nickel Chloride, NiCl <sub>2</sub> 6H <sub>2</sub> O, g. Per Litre.	Potassium Chloride, KCl, g. Per Litre.	Boric Acid, H <sub>3</sub> BO <sub>3</sub> , g. Per Litre.	Other Constituents, g. Per Litre.
NSB . KC (N) NSB . C NSA . KC (Y) NSB . KCF (F)	240 210 120	30.3	19 8	30 30 	Ammonium Sulphate, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , 21. Sodium Chloride, NaCl, 7.85. Sodium Fluoride, NaF, 5.8.

<sup>&</sup>lt;sup>3</sup> "'Stopping Off' Materials for Use in the Electrodeposition of Nickel," D. J. Macnaughtan and A. W. Hothersall, *Trans. Faraday Soc.*, **26**, 163, 1930.

nickel, S sulphate, B borate, K potassium, C chloride, F fluoride and A ammonium. Three of the solutions have been denoted in previous communications 1, 4 by different symbols; these are added in brackets.

#### Deposition.

The deposits were prepared in rectangular glass jars  $10\frac{1}{2} \times 9\frac{1}{2} \times 16$  ins. deep containing about 17 litres of solution which were maintained at 35° C.  $\pm$  1° by immersion in a thermostatically controlled water bath. One anode was arranged on each side of the central cathode in such a manner that the current density on the latter was approximately uniform and II amperes per sq. ft. Deposition was continued for approximately 120 hours, the acidity of the solution being checked and controlled at frequent intervals by colorimetric determinations of the  $p_{\rm H}$  value of the solution. The values given throughout this report are corrected, by the deduction of the "Salt error" (0·2  $p_{\rm H}$  units for solution NSA . KC, 0·5  $p_{\rm H}$  units in all other cases, in the range  $p_{\rm H}$  3 upwards), to the quinhydrone electrode values.

After deposition the cathodes were removed from the bath and washed, the edges were sawn off and the deposit separated from the basis metal. The thin film of copper and copper sulphide remaining on the back of the nickel deposit was removed by immersion in dilute nitric acid.

Four strips 3 ins. long by r in. wide were cut from each deposit; two were used for the determination of the mechanical properties of the metal as deposited, the remaining pair being annealed. The respective specimens were cut from the same portion of each deposit and with the longer axis parallel to the surface of the solution during deposition.

#### Cold Rolled Nickel.

Approximately 100 grms. of nickel prepared from the NSB.C solution at  $p_{\rm H}$  4.9 in an identical manner to the specimens examined was melted in a high frequency furnace, deoxidised with 0.3 per cent. of 60: 40 Mg. Ni and cast into an ingot. A portion of this ingot was cold rolled to the maximum obtainable hardness (Brinell number 209) and its micro-structure examined. It was subsequently treated with the deposited specimens and its microstructure examined after annealing. The ingot contained a large amount of dispersed non-metallic matter, which had not segregated due to the rapid cooling subsequent to casting.

#### Annealing of Specimens.

When thin strips of nickel are heated in air, particularly at temperatures exceeding 400° C., intercrystalline penetration of oxygen takes place with embrittlement of the specimen. The annealing treatment was therefore carried out in vacuo at a pressure of less than 0.01 mm. of mercury, in a Pythagoras composition tube heated in a tubular electrical resistance furnace. During the initial period of the treatment considerable amounts of gas were liberated from the metal. A temperature of 1000° C.  $\pm$  10° C. was maintained for 4 hours after which the specimens were allowed to cool before air was admitted. Upon removal from the tube the specimens were bright and free from oxide tarnish.

# Examination of the Microstructure.

The microstructure of the deposits was examined both before and after annealing, the strips being mounted for the purpose edgewise in Wood's alloy and polished. After annealing the polished but unetched surface was examined under a microscope. Subsequently the strips were removed

<sup>4</sup> "The Influence of Small Amounts of Chromic Acid and Chromium Sulphate on the Electrodeposition of Nickel," D. J. Macnaughtan and R. A. F. Hammond, *Trans. Faraday Soc.*, 26, 481, 1930.

from the fusible alloy and etched in a mixture of 600 c.c. nitric acid (S.G. 1·42), 300 c.c. glacial acetic acid and 300 c.c. of water.

#### Determination of Mechanical Properties.

- 1. Brinell Hardness.—The face of each specimen was ground to a smooth surface, especial care being taken to avoid overheating, and both the face and back further polished with fine emery paper. Two determinations of Brinell hardness were made on the face and two on the back of each strip with a 1 mm. ball and a 10 kg. load. Further tests were made after annealing.
- 2. Tensile Strength and Elongation.—For the determination of the ultimate tensile strength and elongation the strips, which had already been ground to a smooth surface, were formed into flat test pieces, the width and length of the parallel portion being half an inch and one inch respectively; extensions were measured on a gauge length of one inch. Deposits prepared from the NSB . KC and NSA . KC solutions at the highest  $\rho_{\rm H}$  were too brittle to form into test pieces.

#### Results.

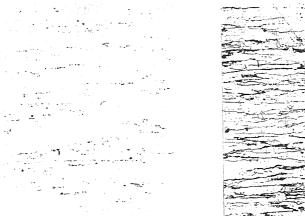
#### I. Microstructure.

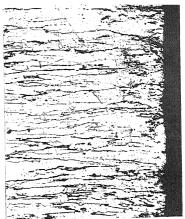
Small black specks were visible in all the polished unetched specimens. In view of their small number and irregular arrangement in certain of the samples, these might have been considered to be matter accidentally introduced into the surface during polishing. In other cases, however, the number and orderly disposition of these black specks (Fig. 1) show that they cannot be explained except as actual non-metallic inclusions in the metal. In the etched specimens this black material is seen to be grouped along the boundaries of crystals.

The microstructure of the etched specimens is shown in Figs. 2, 3, 4, 5 and 6.

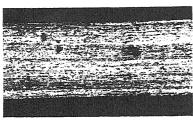
NSB.KC Solution (Fig. 2). — Deposits prepared in the NSB.KC solution showed before annealing a structure composed, except at the highest  $p_{\rm H}$  values, of coarse needles with their long axes normal to the plane of the basis metal. Examination of the structure of the annealed deposits showed that recrystallisation into medium-sized equiaxial grains had occurred in the case of the deposit produced at  $p_{\rm H}$  2.5. Above this  $p_{\rm H}$  some retention of the original structure could be observed, the similarity increasing with rise in  $p_{\rm H}$ ; the grain boundaries of these deposits were found to be composed in general of a layer of non-metallic matter which was visible in the surface of the unetched specimens and had apparently been produced by the aggregation of material derived from the breakdown of films of included material during growth of the needle-like crystals in the course of heat-treatment. The segregated non-metallic matter was present in bands approximately normal to the cathode surface; it would thus appear likely that the original crystals were continuous through the thickness of the deposit or alternatively that the obstruction to grain growth was less in a direction normal to the cathode than in a direction parallel to it. In the deposits formed below  $p_{\rm H}$  2.5 the amount of included non-metallic material was sufficient to restrict grain growth during annealing to some extent. The structure of the deposit prepared at the highest pH value was so small that it could not be readily observed; numerous cracks were present. Little evidence of crystallisation or grain growth was obtained on annealing this deposit; this would appear to be due to the very large amount of included material present.

**NSB. C Solution** (Fig. 3).—A striking change in structure was produced on annealing deposits prepared in the NSB. C solution, which differs from the NSB. KC solution only in the absence of potassium ions. Whilst the structure of the annealed deposits prepared at the highest  $p_{\rm H}$  values

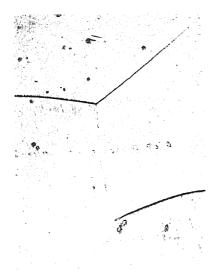


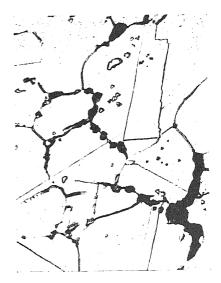


Unetched  $\times$  80 Etched  $\times$  80 Fig. 7.—Structure of deposit prepared in solution NSB . KC at  $p_{\rm H}$  4.9 after heat-treatment,

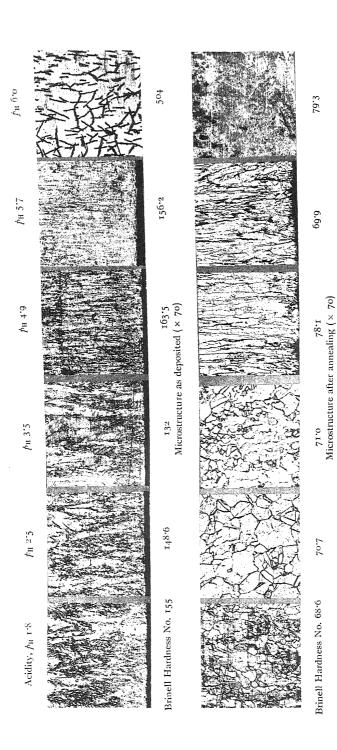


Brinell Hardness No. 209. Brinell Hardness No. 603. Before annealing ( $\times$  80). After annealing ( $\times$  80). Fig. 5.—Hard-rolled cast electrolytic nickel.

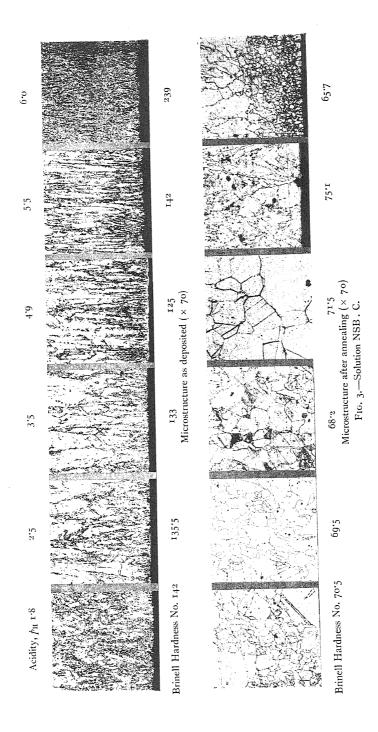


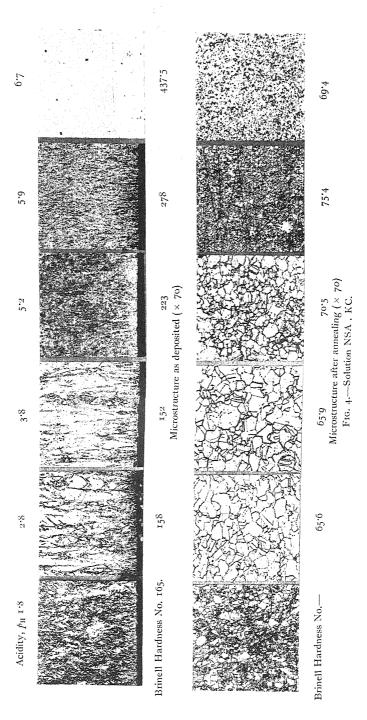


Solution NSB . C  $\dot{p}_{\rm H}$  4'9. Solution NSA . K C  $\dot{p}_{\rm H}$  5'2. Fig. 6 —Grain boundaries after annealing (× 800). [To face page 758.



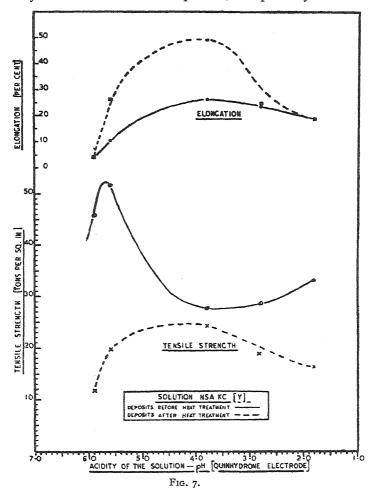
Frg. 2.-Solution NSB . KC.





showed some restriction of grain growth in a direction parallel to the basis metal, the interference was less than in deposits prepared in the other solutions. The grain size after annealing of deposits prepared below the critical  $p_{\rm H}$  ( $p_{\rm H}$  5.0), notably that prepared at  $p_{\rm H}$  4.9, was large and comparable with that of the melted and annealed specimen (see Fig. 5).

NSA. KC Solution (Fig. 4). — The grain size of deposits prepared in the NSA. KC solution above  $p_{\rm H}$  5.0 was small before treatment and less definitely oriented than in other deposits. It is probably for this reason



that after annealing the grains were found in all cases to be equiaxial and polygonal. Their size, however, varied markedly with the acidity of the solution from which they were prepared and was largest in deposits prepared at  $p_{\rm H}$  2.8 and 3.8. Segregated black matter was evident in the unetched annealed specimens and appeared to vary inversely in amount with the grain size.

Examination at high magnification of annealed deposits produced in the NSA. KC bath showed that where the grains were small and their growth had been markedly restricted the boundaries were irregular, contorted and wide; in cases where more normal grain growth (e.g., in NSB.C

solution) had occurred the boundaries are seen to be sharp, clear cut and straight (Fig. 6).

**NSB.** KCF Solution.—Similar results were obtained with deposits from this solution to those observed with deposits from NSB. KC solution with the exception that the retention of the original structure after annealing was only obvious above  $p_{\rm H}$  3.5.

#### 2. Mechanical Properties.

The Brinell hardness of the outer face and that of the back of the deposit prepared at a high  $p_{\rm H}$  were found to be similar; in the softer deposits, however, the first deposited side was invariably harder than the

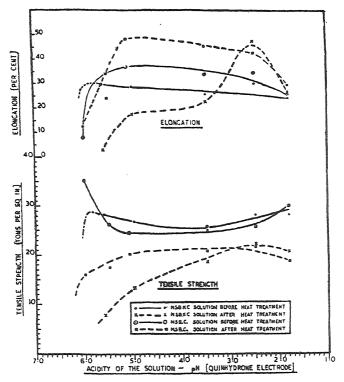


Fig. 8.

outer face. This is related to the progressive coarsening of the crystal structure with increasing thickness. The relationship between hardness of deposits and bath acidity found for the various solutions was in good agreement with the previous determinations.

Some deviation between the results of individual tests on the annealed specimens was observed and the average values did not appear to vary systematically with the  $p_{\rm H}$  of formation of the original deposit. The hardness of all the deposits was, however, reduced by the heat-treatment to between the limits of 65 and 80 Brinell hardness number.

The tensile strength and elongation of deposits are shown graphically in Figs. 7 and 8. Two strips from each deposit were tested and good agreement was in general obtained between the results; the average value has been plotted in each case. The high ratio between the width and thickness of the specimens together with slight variations in the structure,

are unfavourable to the attainment of exactly reproducible results; a further source of error was the non-homogeneity of some test pieces due to the progressive change in structure with thickness, to which reference has been made above. For these reasons the results are regarded as comparative rather than absolute.

The fractures of the more ductile specimens were, in general, at an angle of 45°-60° with the axis of the test piece and showed considerable reduction of cross-sectional area, whilst the more brittle specimens frac-

tured abruptly, the broken ends being jagged and crystalline.

Tensile tests were not made on the deposits from the NSB. KC and NSA. KC solutions at the highest  $p_{\rm H}$  investigated owing to the tendency

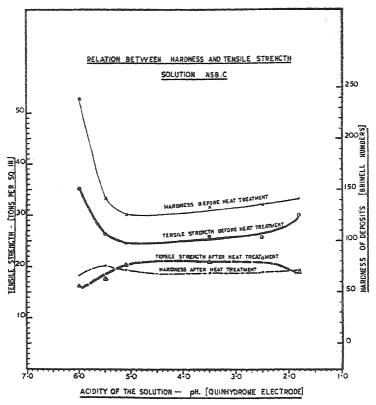


Fig. 9.

of the deposits to be unsound and to contain cracks. It is probably chiefly for this reason that the results obtained show an initial rise in tensile strength with decrease in  $p_{\rm H}$  in the case of these two solutions. With further decrease in  $p_{\rm H}$  the tensile strength falls to a minimum value at moderate  $p_{\rm H}$  in all solutions and then slightly increases; at the same time the ductility rises to a maximum and then falls. The initial decrease is marked in the NSA . KC solution but is more gradual in the other two baths. The deposits from the NSB . C solution show in general a lower tensile strength and a higher elongation than the corresponding deposits from NSB . KC solution.

The tensile strength of all the deposits is considerably reduced by annealing; with decreasing  $p_H$  it rises to a maximum at a moderate

 $p_{\rm H}$  and then slightly falls. Thus a reversal of the results prior to the heat-treatment is found. The elongation of the annealed deposits prepared at high  $p_{\rm H}$  is low, but with decreasing  $p_{\rm H}$  it increases rapidly in the case of solutions NSB . C and NSA . KC, but much more slowly in solution NSB . KC, to maximum values in excess of those found for the untreated deposits ; the elongation then decreases with further decrease in  $p_{\rm H}$  to the lowest value studied.

The variation of the tensile strength of the untreated deposits with  $p_{\rm H}$  is in agreement with the variation of Brinell hardness except at the highest and lowest  $p_{\rm H}$  values (Fig. 9), whilst the elongation varies inversely with the strength.

It is thus clear that the mechanical properties of nickel deposits are

related very closely to the Brinell hardness over a wide range of  $p_{\rm H}$ .

The low values of the tensile strength and elongation of deposits prepared at a high  $p_{\rm H}$  can be related to the large amount of basic material present and to the presence in some deposits of defects such as cracks. There is also evidence that such deposits are already in a state of considerable internal stress; thus the value of the externally applied force necessary to initiate fracture is correspondingly reduced.

#### Discussion of Results.

Macnaughtan and Hammond in studying the influence of acidity on the structure and hardness of electrodeposited nickel, found that in the NSB. KC and NSA. KC solutions (see note to Table I.) a high  $p_{\rm H}$ favoured the formation of deposits having a finely crystalline structure whilst a low  $p_H$  resulted in the production of soft deposits having a larger grain size. The hardness of the deposits was not found to decrease uniformly as the  $p_{\rm H}$  was decreased from the highest value employed. In each solution there was a rapid fall in hardness to a critical  $p_H$  below which a small increase in hardness occurred with further decrease in  $p_{\rm H}$ . The critical  $p_{\rm H}$  values at the current density used were as follows: NSA . KC solution  $p_{\rm H}$  4.7, NSB . KC solution  $p_{\rm H}$  5.3. It was concluded that the striking rise in hardness which occurred above the critical  $p_{\rm H}$ could only be satisfactorily explained by the co-deposition of nickel hydroxide or a basic salt; this suggestion has been confirmed and elaborated in the case of other nickel depositing solutions in the preceding paper (see page 729). In the present investigation the results of examination of annealed deposits substantiate this view to a marked degree.

Thus the amount of visible inclusions and the degree to which crystal growth has been restricted are related to the Brinell hardness number of the deposits as prepared. For example the annealed deposits prepared in the high  $p_{\rm H}$  range above the critical  $p_{\rm H}$  show strong evidence, in the case of all the solutions examined, that co-deposition of basic material has occurred, since in all cases there is restriction of grain growth accompanied, to a varying degree, by the segregation of black material in the grain boundaries; the corresponding unannealed deposits were in all cases hard. With reduction in solution  $p_{\rm H}$  resulting in the production of softer deposits, the evidence of restricted grain growth and segregation of black material is reduced. In the case of the NSB. C solution, which gave the softest deposits of all the solutions used, large equiaxial crystals were observed in the annealed specimens produced at  $p_{\rm H}$  4.9 and there was very little evidence of interference with grain growth or of segregated matter. The addition of potassium to this

solution (to form NSB.KC) results in the production of consistently harder deposits in the  $p_{\rm H}$  range below the critical  $p_{\rm H}$ ; the corresponding annealed specimens possess a smaller grain size and show signs in some cases of the original crystal orientation, thus indicating restriction of grain growth.

Furthermore the black segregated matter is visible both before and after etching in the annealed deposits (see Fig. 1). The manner in which grain growth has occurred and the disposition of the segregated matter after heat-treatment suggests that the basic material was originally present in the form of thin and invisible films coating each grain of the original deposit. Thus where the original grains consisted of long needles, the annealed deposit in some cases shows retention of this type of structure, the new grain boundaries apparently containing large quantities of segregated matter (Fig. 2,  $p_{\rm H}$  4.9 and 5.7).

In the case of the rolled nickel, however, large almost equiaxial polygonal grains were produced on annealing. Although similar equiaxial crystals were obtained in annealed deposits produced at  $p_{\rm H}$  4.9 from the NSB. C solution, showing that there was very little interference with grain growth, this does not necessarily imply the complete absence of basic material in the deposit since it is probable that nickel has a definite solubility for this material; solution would take place on heating the deposit initially, which might in the case of a small concentration of the material result in the almost complete removal of any interference with crystallisation.

In general, therefore, the results obtained in this investigation confirm the correctness of the previous deductions that the cause of the high hardness of nickel deposits is due to the co-deposition of basic material.

It is evident that the presence of basic material in the original deposits, which largely determines their physical properties, is likely to have a more pronounced effect on the metal in the annealed condition. This effect will be in part due to the restrictive action upon grain growth which influences the final grain size and orientation obtained, and also to the presence of segregated matter at the crystal boundaries, which is likely to diminish the ductility of the deposits. The latter effect will tend to be most pronounced in cases where as a result of the original structure of the deposit, segregation of the included matter forms almost continuous bands across the deposit. Thus, in such cases it has been found that propagation of a crack tends to proceed easily along the layer of nonmetallic matter. This is indicated by results of mechanical tests which reveal the low tensile strength and elongation of the annealed deposits produced at high  $p_{\rm H}$  where the maximum amount of basic material would be expected to be present (Figs. 7 and 8). This form of brittleness is most pronounced in annealed deposits from the NSB, KC solution in which preferential orientation of the grains in a direction normal to the original cathode face tends to be pronounced in deposits produced in the  $p_{\rm H}$  range above 3.5. In the case of the NSA. KC solution, a large amount of basic material may be present without the same preferential concentration in bands on annealing since it is more distributed around smaller crystals; consequently while brittleness has been induced, there are not such continuous planes of weakness as in deposits from the NSB. KC solution.

Information is being sought concerning the composition of the basic material in the deposit. Although there is a strong probability that hydroxide of nickel is discharged from the sol form to the neutral form at the growing crystal face it is possible that at the moment of discharge the hydroxide is changed to oxide with the loss of water (Hunt 5).

### Summary and Conclusions.

Previous investigations on the cause of the hardness of electrodeposited nickel have suggested that basic material is co-deposited under all conditions of deposition but in amounts varying with the composition and acidity of the depositing solution. Further evidence for this view has been obtained as a result of examination of the Brinell hardness, ultimate tensile strength, elongation and microstructure of deposits prepared from a number of solutions at various acidities, before and after annealing for four hours at 1000° C. in vacuo.

It has been found that the Brinell hardness and the tensile strength of the unannealed deposits are closely related, except in the presence of defects such as cracks, and are in accordance with the microstructure; the elongation is also approximately inversely proportional to the tensile

strength.

The manner in which grain growth of the deposits occurs during annealing is found to be related to the original structure and Brinell hardness; considerable restriction of grain growth due to segregation of non-metallic material has been observed in certain cases, particularly with deposits produced in conditions which would be expected to result in the inclusion of a relatively large amount of basic material.

The tensile strength and elongation of the annealed deposits are found to be much reduced in some cases by the non-metallic material and to a lesser extent in others, according to its amount and disposition. It is considered that the segregated non-metallic matter results from the aggregation during annealing of basic material co-deposite on the crystal boundaries; this material although invisible in the original deposits, is regarded as likely to be present in all nickel deposits and is considered to be the cause of the higher hardness of such deposits as compared with that of the metallurgically produced annealed metal.

The significance of the results is discussed in the light of the theory of nickel deposition previously put forward.

The authors desire to extend their thanks to Mr. H. Wrighton, B.Met., for the preparation of the photomicrographs.

<sup>5</sup> "A Study of the Structure of Electrodeposited Metals," L. B. Hunt, J. Physic Chem., 36, 1006, 1932.

# THE ACTION OF POTASSIUM CYANIDE SOLU-TIONS ON COLLOIDAL GOLD.

By F. P. Worley and E. D. Robins.

Received 27th March, 1933.

The action of alkali cyanides on gold has been the subject of numerous investigations, the most exhaustive probably being that of Maclaurin <sup>1</sup> who confirmed the equation suggested in 1846 by Elsner, viz.,

$$4 \text{ Au} + 8 \text{KCN} + O_2 + 2 \text{H}_2 \text{O} = 4 \text{ KAu}(\text{CN})_2 + 4 \text{ KOH}.$$

The necessity for oxygen had been thrown into doubt, but Maclaurin showed that in the absence of oxygen no gold was dissolved. The

<sup>1</sup> Trans. Chem. Soc., 63, 724, 1893.

potassium cyanide was found to have maximum activity at a concentration of 0.25 per cent., the lower activity at higher concentrations being shown to be due to the lower solubility of oxygen in the more concentrated solutions. Bodländer 2 confirmed the necessity for oxygen and showed that when spongy gold was dissolved by dilute solutions of potassium cyanide in the presence of air, the oxygen was converted first into hydrogen peroxide by an action considered analogous to that of the production of hydrogen peroxide in the dissolution of zinc by caustic potash in the presence of oxygen 3. He represented the action as taking place in two stages, viz.,

Michailenko and Meschtscherjakoff 4 investigated the effect of various added substances on the rate of dissolution of gold by solutions of potassium cyanide. They found that certain oxidising agents particularly salts of per acids, sodium peroxide and potassium ferricyanide accelerated the action, that sodium chloride and mercuric cyanide had no influence, that hydrogen ions retarded and eventually stopped the action and that hydroxyl ions exerted a retarding influence. Andréev 5 found that when oxygen was passed at constant rate through solutions of potassium cyanide in the presence of gold the rate of dissolution increased with increasing concentration of cyanide up to 0.3 per cent. and thereafter decreased. Ozone and hydrogen peroxide at low concentrations increased the rate but at higher concentrations retarded the action, the gold becoming coated with a red layer of oxide. With manganese dioxide or lead dioxide in the presence of ozone or hydrogen peroxide the rate was greatly increased. Reichinstein 6 from consideration of Andréev's observations attempted an electrochemical explanation of the action of oxygen, postulating the formation of a gold-oxygen alloy. His explanation, however, did not take account of Bodländer's observations. Worley? from preliminary observations considered that in the dissolution of gold by solutions of potassium cyanide the primary action was the formation of aurous cyanide and hydrogen peroxide by interaction of gold, oxygen and hydrocyanic acid formed by hydrolysis of the cyanide, the action being analogous to that of dilute sulphuric acid on copper in the presence of oxygen.8 The action was expressed by the equations

$$2 \text{ Au} + 2 \text{HCN} + \text{O}_2 = 2 \text{ AuCN} + \text{H}_2\text{O}_2$$
  
 $2 \text{ Au} + 2 \text{HCN} + \text{H}_2\text{O}_2 = 2 \text{ AuCN} + 2 \text{H}_2\text{O}.$ 

A difficulty experienced by Maclaurin and by subsequent investigators was the considerable variation in the amount of gold dissolved under apparently identical conditions, probably due to variation in the surface condition of the gold. The use of precipitated gold has been advocated but gold sols would appear to offer greater uniformity. With sols produced under different conditions or having different histories considerable variations are to be expected, but different samples of any given preparation should yield uniform results under similar conditions.

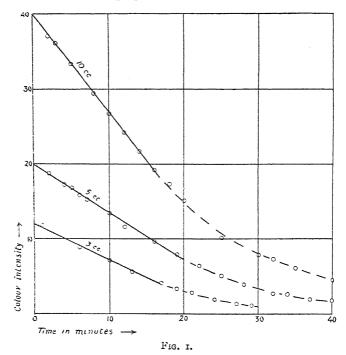
 <sup>&</sup>lt;sup>2</sup> Z. angew. Chem., 9, 583, 1896.
 <sup>3</sup> Traube, Ber., 18, 1877,
 <sup>4</sup> J. Russ. Phys. Chem. Soc., 44, 567, 1912.
 <sup>5</sup> Z. Elektrochem., 19, 667, 1913.
 <sup>6</sup> Ibid., 672, 1913.
 <sup>7</sup> Australasian Assoc. for the Advancement of Science, 16, 228, 1923. <sup>3</sup> Traube, Ber., 18, 1877, 1885.

<sup>&</sup>lt;sup>8</sup> Traube, Ber., 18, 1887, 1885.

From preliminary experiments it was found that unprotected sols. not dialysed, were decolorised by potassium cyanide much more rapidly than when protected by gelatin. Increase in the amount of gelatin beyond the minimum necessary to prevent precipitation during dialysis had relatively little further effect in reducing the rate of interaction. Several gold sols, prepared by different methods, were protected by the minimum amount of gelatin and dialysed. The rate of dissolution of the gold by potassium cyanide under similar conditions varied widely for different preparations, due apparently to differences in the degree of dispersion. Highly dispersed sols prepared by reduction with phosphorus were decolorised by potassium cyanide very much more rapidly than less highly dispersed sols prepared by reduction with formaldehyde or hydrazine. From the various sols prepared three were selected for further use, a blue sol and a purple blue sol prepared by reduction with hydrazine hydrochloride and a red sol prepared by Zsigmondy's formaldehyde method.

#### Determination of Rate of Interaction.

The potassium cyanide used contained 95.5 per cent. KCN and 4.5 per cent. free KOH and was free from carbonate. An approximately decinormal solution was prepared with carbon dioxide free water and



protected from the air. The course of the interaction with the colloidal gold was followed by means of a colorimeter at room temperature, the reference solution being made up with the same amount of colloid as the reacting solution, appropriately diluted with distilled water.

It was found, in general, that the colour intensity, measured by the colorimeter readings, when plotted against the times gave a straight line for approximately the first half of the change. In the case of some preparations of colloid the straight line continued for more than three-quarters of the change before the rate of reaction began to slow down. The progress of the interaction is thus closely analogous to that frequently observed in the case of enzyme action.

With different initial concentrations of colloid and the same concentration of cyanide the slope of the curves was approximately the same when the concentration of colloid in the reference solution was the same as that in the reaction solution. The rate of reaction, as measured by the reduction of colour intensity, is thus proportional to the number of colloid particles, which does not become appreciably diminished during the first half or three-quarters of the change. It is to be expected that smaller particles would be dissolved more rapidly than larger particles, and this was borne out by the observation that the purple-blue sol became bluer as the reaction proceeded due presumably to the preferential removal of the more highly dispersed red constituent of the sol. The results for three concentrations of colloid with one concentration of potassium cyanide are shown graphically in Fig. 1.

#### Effect of Concentration of Cyanide.

In a series of experiments in which the initial concentration of colloid was the same and the concentration of potassium cyanide varied, the rate of reaction, measured by the colour change, increased more rapidly than the concentration of cyanide. The concentrations used were 5 c.c. of gold colloid and from 2 to 10 c.c. of decinormal potassium cyanide made up to 20 c.c. The results are given in Table I.

TABLE I.

KCN.		Rate.	Rate/C.c.	
C.c. N/10.	Per Cent.		KCN.	
2 3 4 5 6 7 8 9	0.065 0.098 0.131 0.164 0.196 0.229 0.262 0.262	1·28 2·16 3·08 4·89 6·12 8·26 1·00 13·5 16·2	0.64 0.72 0.77 0.98 1.02 1.18 1.25 1.50	

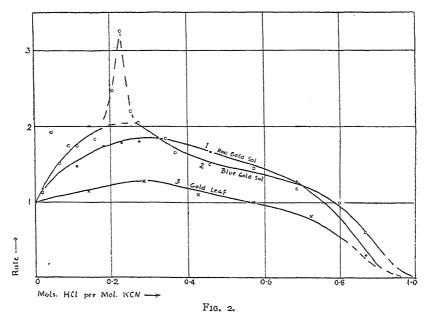
The rate for the more concentrated solutions was difficult to determine accurately on account of the rapidity of the change. There was no maximum observed however at a concentration of cyanide of 0.25 per cent. as found by Maclaurin when using the metal itself.

#### Effect of Addition of Hydrochloric Acid.

Numerous series of experiments were carried out in which the initial amounts of colloid and cyanide were the same for each series and varying amounts of hydrochloric acid, up to an amount equivalent to the cyanide were added, the total volume being made the same throughout. For example, in several series of determinations the amounts used were, in order of addition, distilled water sufficient to make the final volume 20 c.c., 2 c.c. N/10 KCN, up to 40 drops of N/10 HCl and finally 5 c.c. of gold sol. In each series, addition of hydrochloric acid, with consequent liberation of hydrocyanic acid, was accompanied by marked increase in the rate of reaction until an amount of acid equivalent to

about one-third of the cyanide was added. Larger amounts of hydrochloric acid had progressively less effect, the rate being finally reduced to zero when the added acid was equivalent to the cyanide. Curves representing two typical series of determinations are shown in Fig. 2 in which the rates correspond to unit rate in the absence of hydrochloric acid. The actual rates for zero concentration of acid differed for different sols. Curve I, representing a series of determinations with a bright red sol, is typical of many obtained both for red and for blue sols. Curve 2 (blue sol) shows a very sharp maximum observed in a limited number of cases, the greatly increased rate at certain concentrations of added acid being apparently due to some condition of the colloid which we have not determined.

These results are in apparent agreement with a mechanism involving the initial interaction of gold and hydrocyanic acid. In the absence of



added acid sufficient hydrocyanic acid, formed by hydrolysis, is present to cause a moderate rate of reaction, the rate increasing with addition of hydrochloric acid and consequent liberation of hydrocyanic acid. In the absence of oxygen interaction with the gold to form aurous cyanide would involve liberation of hydrogen, an action which might be possible with a highly dispersed gold sol. This possibility could be arrived at from a knowledge of the heats of formation of hydrocyanic acid and aurous cyanide and the total surface energy of the colloidal gold. Oxygen, however, appears to be necessary in the case of colloidal gold as in the case of the metal itself. In an experiment in which oxygen was removed by boiling under reduced pressure before mixing the solutions in a divided vessel there was no appreciable change of colour during a considerable interval after mixing. When air was admitted however, the action proceeded normally. The probable initial formation of aurous cyanide is supported by experiments in which an amount of hydrochloric acid equivalent to the cyanide was added. After the

solution had remained for some time without apparent change the addition of a small amount of potassium cyanide resulted in a rate of reaction greater than that corresponding to this amount of cyanide used alone.

### Experiments with Gold Leaf.

Although gold leaf cannot be used as conveniently as colloidal gold, experiments were carried out in order to ascertain whether the general phenomena observed in the case of colloidal gold occurred with the metal itself. It was observed that finely divided gold leaf could not at first be made to sink in the cyanide solution. After an interval, however, as action proceeded, the gold leaf sank in the solution, the initial floating being apparently due to a film of adsorbed oxygen which was gradually removed as the action of the cyanide proceeded. In the experiments on the rate of dissolution in potassium cyanide solution, equal amounts of gold leaf were taken and finely divided by grinding with a small amount of potassium chloride crystals. Water was added, the solutions boiled till the metal sank, and the salt removed by repeatedly diluting and pipetting off the supernatant liquid. The rate of dissolution of the gold by dilute potassium cyanide solution in the presence of different amounts of hydrochloric acid was determined in terms of the reciprocals of the times of equal amounts of change. The results of one series of experiments are shown in curve 3, Fig. 2, and are seen to be in general agreement with those obtained with colloidal gold.

#### Effect of Addition of Alkali.

If the primary interaction is between gold and hydrocyanic acid it should follow that the addition of potassium hydroxide should, by depressing the degree of hydrolysis, reduce the rate of reaction. It was found that the addition of small amounts of potassium hydroxide reduced the rate of dissolution of colloidal gold but with further addition, up to amounts equivalent to the cyanide, there was in some cases no further change in the rate whilst in other cases the rate increased slightly with increased concentration of alkali. In carrying out the determinations it was found that the addition of alkali alone to the gold sol produced an immediate small colour change. The reference solution was consequently prepared containing potassium hydroxide of concentration equal to that of the added alkali in the test solution.

In the case of gold leaf the addition of caustic potash at first slightly reduced the rate of dissolution but larger amounts caused a definite increase in rate, considerably greater than that observed in any of the experiments with colloidal gold. Michailenko and Meschtscherjakoff,<sup>4</sup> on the other hand, found that excess of alkali exerted a retarding influence on the rate of dissolution of gold by dilute solutions of potassium cyanide.

#### Conclusion.

The above experimental results appear to us to show that the main primary action in the dissolution of gold by dilute solutions of potassium cyanide is the interaction of gold and hydrocyanic acid in the presence of oxygen. The production of hydrogen peroxide, accompanying the dissolution (Bodländer) indicates that the oxygen acts mainly in the molecular condition, either dissolved in the solution or adsorbed in molecular condition on the surface of the gold. The relatively insoluble aurous cyanide formed in the primary action then combines

with potassium cyanide to form the easily soluble double cyanide. Accordingly the mechanism of the main reaction should, we consider, be expressed by the following equations which together are equivalent to the original equation of Elsner, confirmed by Maclaurin.<sup>1</sup>

$$4KCN + 4H_2O = 4KOH + 4HCN$$

$$2Au + 2HCN + O_2 = 2AuCN + H_2O_2$$

$$2Au + 2HCN + H_2O_2 = 2AuCN + 2H_2O$$

$$4KCN + 4AuCN = 4KAu(CN)_2$$

$$4Au + 8KCN + 2H_2O + O_2 = 4KAu(CN)_2 + 4KOH$$

It is improbable, however, that the dissolution occurs entirely in this way. In the case of colloidal gold there is some evidence that the colloidal particles are covered by a molecular layer of a hydrated gold oxide or of auric acid. This in the presence of alkali would be converted to oxide which would interact with cyanide solution without the production of hydrogen peroxide. The small colour change observed on adding alkali to gold sol is in harmony with the possibility of the initial stage of dissolution of colloidal gold occurring in this manner. Again the effect of the addition of alkali except in very small amounts, in the case both of colloidal gold and of gold leaf does not appear to be in agreement with the mechanism suggested for the main action. Possibly, however, the alkali affects the availability of oxygen.

In the technical extraction of gold by the cyanide process the rate of extraction is not the only factor to be considered, and a degree of "protective alkalinity" greater than that corresponding to the maximum rate of reaction may be desirable. By a modification of the methods described above it should be possible rapidly to measure the reactivity of the technical solutions employed and thus more easily control the process.

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# THE MECHANISM OF HYDROGEN OVERVOLTAGE AND OF THE ELECTROLYTIC OXIDATION OF HYDROGEN.

By Louis P. Hammett.

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The relation between current and potential on cathodes on which hydrogen is being evolved at high overvoltages has been established with certainty and precision by the work of Bowden.<sup>1</sup> His results may be summarised in the equation

$$I = -k \exp\left(-\frac{\text{o.5F}\Delta E}{RT}\right) \qquad . \qquad . \qquad (1)$$

Here  $\Delta E$  and I are overvoltage and current, both taken negative for cathodic polarization; and the constant k is a function both of the nature of the cathode metal and of the temperature, but is independent of the hydrogen ion concentration of the solution.

<sup>&</sup>lt;sup>1</sup> Bowden and Rideal, *Proc. Roy. Soc.*, **120A**, 59, 80, 1928; Bowden, *Trans. Faraday Soc.*, **24**, 473, 1928; *Proc. Roy. Soc.* **126A**, 107, 1929; Bowden and O'Connor, *ibid.*, **128A**, 317, 1930.

Theoretical derivations of this equation, including the factor 0.5 without which it would be almost obvious, have recently been given by Gurney, and by Erdey-Grusz and Volmer. Frumkin has made the interesting suggestion that this factor has the same origin as the fractional exponent in the Brönsted equation for general acid or basic catalysis. Common to all of these discussions is the hypothesis that the reaction

$$H^+ + e \rightleftharpoons H$$
 . . . (I)

is the rate controlling step in the electrolytic evolution of hydrogen-The same hypothesis has been adopted by Brönsted and Kane 6 in discussing the evolution of hydrogen by reaction of sodium amalgam with acids.

When, however, the reaction

$$2H^+ + 2e \rightleftharpoons H_2$$

is studied on electrodes such as catalytically active platinum which permit the measurement of current at very low overvoltages and for the oxidation of hydrogen as well as for the reduction of hydrogen ion, it is found that the results for small polarizations can be represented by the equation 7

$$I = k \left\{ I - \exp\left(-\frac{2F\Delta E}{RT}\right) \right\}$$
$$-0.0I < \Delta E < +0.0I \qquad . \qquad . \qquad (2)$$

This equation has been derived from the assumption that the rate determining step is

$$2H \rightleftharpoons H_0$$
 . . . (II)

In fact it is only possible to account for the course of positive polarizations (in which hydrogen is oxidised) by supposing that the rate determining step is some reaction such as the dissociation of molecular hydrogen which is not directly affected by the electrode potential.

It is possible to reconcile these conflicting aspects of the hydrogen evolution reaction and to account quantitatively for the rate of hydrogen evolution on platinum at polarizations outside the range covered by equation 2 by admitting that both of the steps I and II are significant in determining the rate of the total reaction, and that the rate in the forward direction of step I is given by equation I with the factor 0.5. The complete expression for the current must, however, contain another term representing the rate of the reverse reaction in order to satisfy the requirement that I shall become 0 when  $\Delta E$  becomes 0, as Butler,<sup>2</sup> and Erdey-Grusz and Volmer 4 have shown. The equation

$$I = k_1[H] \exp \left(\frac{F\Delta E}{2RT}\right) - k_2 \exp \left(-\frac{F\Delta E}{2RT}\right)$$
 . (3)

<sup>3</sup> Gurney, Proc. Roy. Soc., 134A, 137, 1931; 136A, 378, 1932; Fowler, Trans.

<sup>&</sup>lt;sup>2</sup> Tafel, Z. physik. Chem., 34, 200, 1900; 50, 649, 1905; Lewis and Jackson, ibid., 56, 193, 1906; Hammett, J. Amer. Chem., Soc., 46, 7, 1924; Butler, Trans. Faraday Soc., 19, 734, 1924; 28, 379, 1932.

Faraday Soc., 28, 368, 1932.

<sup>4</sup> Erdey-Grusz and Volmer, Z. physik. Chem., 150A, 203, 1930. See also Erdey-Grusz and Wick, Z. pyksik. Chem., 162A, 53, 1932.

<sup>5</sup> Frumkin, Z. physik. Chem., 160A, 116, 1932.

<sup>6</sup> Presented and Money I Among Chem. Soc. 22, 2624, 1921. See also Hammett

<sup>&</sup>lt;sup>6</sup> Brönsted and Kane, J. Amer. Chem. Soc., 53, 3624, 1931. See also Hammett and Lorch, *ibid.*, **54**, 2128, 1932, and Frumkin, ref. 5. 7 Hammett, *J. Amer. Chem. Soc.*, **46**, 7, 1924.

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is identical with those proposed by Butler, and by Erdey-Grusz and Volmer except that it takes count of Bowden's finding that the overvoltage is independent of hydrogen ion concentration.8 The rate of change of concentration of atomic hydrogen on the electrode surface must be zero in the steady state and is given by

$$\begin{split} \frac{d[\mathbf{H}]}{dt} &= \mathbf{0} = k_2 \text{ exp.} \left( -\frac{F\Delta E}{2RT} \right) - k_1[\mathbf{H}] \text{ exp.} \left( \frac{F\Delta E}{2RT} \right) \\ &+ k_3[\mathbf{H}_2] - k_4[\mathbf{H}]^2 \quad . \quad (4) \end{split}$$

The first term gives the rate of formation of atomic hydrogen by reduction of hydrogen ion, the second the rate of oxidation to hydrogen ion, the third the rate of dissociation of molecular hydrogen, and the fourth the rate of combination to molecules. Elimination of [H] between equations 3 and 4 gives

$$I^{2}\left\{\frac{k_{4}}{k_{1}^{2}}\exp\left(-\frac{F\Delta E}{RT}\right)\right\} + I\left\{1 + \frac{2k_{2}k_{4}}{k_{1}^{2}}\exp\left(-\frac{3F\Delta E}{2RT}\right)\right\} - k_{3}[H_{2}] + \frac{k_{4}k_{2}^{2}}{k_{1}^{2}}\exp\left(-\frac{2F\Delta E}{RT}\right) = 0 . \quad (5)$$

From the requirement that I = 0 when  $\Delta E = 0$ 

$$k_3[H_2] = \frac{k_4 k_2^2}{k_1^2}$$
 . . . (6)

and by substitution the final equation

$$I^{2} \left\{ \frac{k_{3}[H_{2}]}{k_{2}^{2}} \exp \left( -\frac{F\Delta E}{RT} \right) \right\} + I \left\{ I + \frac{2k_{3}[H_{2}]}{k_{2}} \exp \left( -\frac{3F\Delta E}{2RT} \right) \right\} - k_{3}[H_{2}] \left\{ I - \exp \left( -\frac{2F\Delta E}{RT} \right) \right\} = 0 . \quad (7)$$

is obtained. For large negative values of  $\Delta E$  this reduces to

$$I = -k_2 \exp\left(-\frac{0.5F\Delta E}{RT}\right) \qquad . \qquad . \tag{8}$$

the Tafel-Bowden equation. For small values of  $\Delta E$  it reduces, provided  $k_3[H_2]/k_2$  is not too large, to

$$I = \frac{k_3[H_2]\left\{1 - \exp\left(-\frac{2F\Delta E}{RT}\right)\right\}}{1 + \frac{2k_3[H_2]}{k_2} \exp\left(-\frac{3F\Delta E}{2RT}\right)}.$$
 (9)

and approximately to

$$I = constant \left\{ 1 - \exp\left(-\frac{2F\Delta E}{RT}\right) \right\}$$
 . (10)

which is equivalent to equation 2.

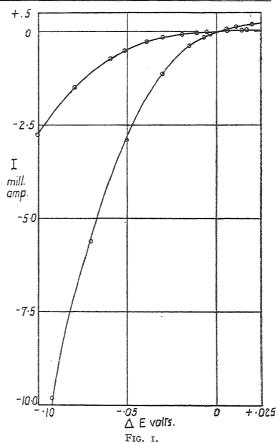
<sup>8</sup> This is equivalent to making the velocity of reduction of hydrogen ion proportional to  $[H^+]^{\frac{1}{2}}$  exp.  $\left(-\frac{FE}{2RT}\right)$ . This equation is in terms of E, the electrodesolution potential difference, instead of  $\Delta E$ , the difference between the actual potential difference during current flow and the potential difference of an equilibrium hydrogen electrode in the same solution. It then becomes necessary that the velocity of the reverse reaction be proportional to  $\frac{[H]}{[H^+]^{\frac{1}{2}}} \exp\left(\frac{FE}{2RT}\right)$ . reason for the fractional exponents does not appear from any of the theoretical discussions.

Table I. shows a comparison of equation 7 with two of the experi-

$\Delta E  imes  ext{io}^3$ $I  ext{ calc.}  imes  ext{io}^3$ $I  ext{ obs.}  imes  ext{io}^3$	-92·2	-70·5	-50·1	-49·9	-30·2	-15·4	-15·2
	-9·92	-5·52	-2·78	-2·77	-1·124	-0·395	-0·392
	-9·80	-5·60	-2·88	-2·89	-1·112	-0·390	-0·390
$\Delta E  imes  ext{IO}^3$ $I  ext{ calc.}  imes  ext{IO}^3$ $I  ext{ obs.}  imes  ext{IO}^3$	-7·02	-3·54	-1·46	+2·11	+5·56	+11.0	+19·7
	-0·146	-0·067	-0·026	+0·034	+0·083	+0.142	+0·204
	-0·140	-0·063	-0·025	+0·033	+0·079	+0.138	+0·200
Experiment 93. $k_2 = 0.0000273$ , $k_3[H_2] = 0.000483$ .							
$\Delta E  imes  ext{Io}^3$ $I  ext{ calc.}  imes  ext{Io}^3$ $I  ext{ obs.}  imes  ext{Io}^3$	-100·7	-79·4	-59·4	-51·3	-39·0	-31·6	-30·3
	-2·75	-1·50	-0·734	-0·521	-0·278	-0·177	-0·164
	-2·75	-1·49	-0·739	-0·519	-0·275	-0·172	-0·164
$\Delta E \times 10^3$ $I \text{ calc.} \times 10^3$ $I \text{ obs.} \times 10^3$	-19·3 -0·072 -0·072	-11·2 -0·031 -0·033	-5·8 -0·014 -0·014	+6·0 +0·0093 +0·0085	+14.0 +0.0177 +0.0175	+0.0139 +0.0139 +16.3	

mental polarisation curves which I obtained 7 some years ago on hydrogen electrodes with platinum catalysts. In experiment 77 the electrode was a bare platinum foil of moderate catalytic activity, and the solution was 0.1 Nhydrochloric acid; in experiment 93 the electrode was electro - deposited platinum of much lower activity, and the solution was O·I N potassium hydroxide. Fig. I represents the calculated curves and experimental points for the same experiments.

The excellent agreement thus obtained with these various electrode and solution properties and for both positive and negative polarisations does not of course prove the correctness of the mechanism upon which the equation was based. It should, however, be noted that no



other equation with any theoretical background has been found which does fit this data in spite of considerable search. If this is the correct mechanism, the rate of hydrogen evolution at high overvoltages is determined by the rate of the reduction of hydrogen ion to atomic hydrogen, provided concentration polarisation is kept small; but the rate of combination of atoms to molecules plays a part of constantly increasing importance as the overvoltage decreases until it becomes the chief factor at low overvoltages and for the reverse reaction, the oxidation of hydrogen to hydrogen ion.

To make the above comparison the two parameters  $k_3[H_2]$  and  $k_2$  had to be fitted to the data. Over the range of small polarizations for which equation 9 holds a plot of

$$\underbrace{1 - \exp\left(-\frac{2F\Delta E}{RT}\right)}_{I}$$

against exp.  $\left(-\frac{3F\Delta E}{2RT}\right)$  must be a straight line of slope  $2/k_2$  and intercept  $I/k_3[H_2]$ . Such a plot turns out to be a quite satisfactory method of obtaining a value of  $k_3[H_2]$ , but is not a sufficiently sensitive measure of  $k_2$ . If, however, the value of  $k_3[\mathrm{H}_2]$  thus obtained is substituted in equation 7 along with the experimental values of  $\Delta E$  and I for a large polarization there is obtained a value of  $k_2$  for each experimental point thus treated. Agreement of these values of  $k_2$  is indeed a satisfactory check on the validity of the equation, especially because a value of  $k_3[H_2]$ obtained from small polarizations is verified by the behaviour of large polarizations.

Table II. gives such a check for the two polarization curves already discussed and for three other curves contained in the same article. The

Expt. No.	k <sub>3</sub> [H <sub>2</sub> ].		k	2•		$\frac{k_3[\mathrm{H}_2]}{k_2}.$
76 77 97 91 93	0.000531 0.000286 0.0000090 0.00030 0.0000273	0.00422, 0.00188, 0.000105, 0.00236, 0.000482,	0·00454, 0·00200, 0·000106, 0·00239, 0·000479,	0.00463, 0.00199, 0.000108, 0.000107 0.00230 0.000487,	0.00472 0.00196 0.000110,	0·117 0·145 0·084 0·128 0·056

TABLE II.

values of  $k_2$  there listed are derived from the experimental points at the largest negative polarizations and are in the order of decreasing polarization. The calculations of Table I. are based upon the average of the  $k_2$ values for the respective curves from Table II.

Values of the constants are not given for experiments 80, 75, 85, and These are the experiments in which the catalytic activity of the electrode, and therefore the current for a given value of polarization, are the greatest. For these the distribution of points in the plot used for the evaluation of  $k_3[H_2]$  was very irregular and no values of the two parameters could be obtained by this or other methods which gave a satisfactory fit for both large and small polarizations. It seems probable that the difficulty here arises from the existence in these cases of a concentration polarization due to insufficiently rapid diffusion of dissolved

molecular hydrogen, and subject to irregular variation as a result of

changes in stirring rate.

It was previously pointed out that these polarization curves can be approximately represented by a one parameter function,  $\Delta E = f(\frac{I}{\bar{k}})$ , over a range considerably wider than that to which equation 2 applies. In order for this to be exactly true it would be necessary that  $k_3[H_2]/k_2$ have the same value for all the curves. This is not the case and the exactness with which equation 7 fits the data indicates therefore that the deviations from this one parameter equation are too large and systematic to be attributable to experimental errors.

A change in the area only of an electrode may be expected to change  $k_2$ , the specific velocity constant for step I, and  $k_3$ , the constant for step II, in the same proportion. The fact that their ratio varies with varying activation of a given platinum surface is further evidence that this variation in activity is not a function of area only, although it may be

largely dependent upon it.

#### Summary.

An equation for the rate in the forward and in the reverse directions of the reaction  $2H^+ + 2e \rightleftharpoons H_2$  has been derived on the assumption that both the step  $H^+ + e \rightleftharpoons H$  and the step  $2H \rightleftharpoons H_2$  are of comparable importance in determining the velocity of the total reaction. For large polarizations the first step becomes dominant, for small polarizations the second. The equation fits very closely the experimental data for currentpotential (overvoltage) curves for this reaction on platinum electrodes.

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# THE ELECTROPHORETIC BEHAVIOUR OF LECI-THIN AND CERTAIN FATS.

By Christopher Williams Price and W. C. M. Lewis.

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Hitherto it has been generally assumed that lecithin, as an amphoteric body, owes its charge, in aqueous dispersion, simply to ionisation of the amphoteric groups; an assumption valid to a considerable extent in the case of proteins.

It is shown in the present work, from a consideration of the electrophoretic behaviour of lecithin and certain simple fats, that the charge on a lecithin dispersion must be composed of two interdependent parts, both of which are of comparable magnitude.

Thus the total charge would appear to be due to (a) adsorption of hydroxyl ions on the surface of the fatty portions of the particles, and (b) to ionisation of the amphoteric groups.

It is possible from a consideration of the data obtained, to reconcile the very low value of the observed 1 isoelectric  $p_{\rm H}$  of lecithin (vide

<sup>1</sup> From the surface tension measurements of Price and Lewis (1929) and from distribution measurements of Fuggii (1923-24), the effective isoelectric point is given as  $p_{\rm H}=2\cdot 7$ , a value which is, furthermore, confirmed by the electrophoretic measurements described in the present work. infra) with the value calculated from approximate values of the dissociation constants of lecithin.

Since lecithin is not soluble in water the value of the dissociation constants cannot easily be obtained by direct titration and one must proceed in an indirect manner.

The dissociation constants Ka and Kb of lecithin have their origin in its glycerophosphoric acid and choline residues. The values of Ka and Kb for lecithin should, therefore, be of the same order as the respective dissociation constants of glycerophosphoric acid and of choline.

The values of the dissociation constants of glycerophosphoric acid have been determined by O. Meyerhof and J. Suranyi (1926) and a determination of the dissociation constant of choline is described below.

# Determination of the Dissociation Constant of Choline and Calculation of the Isoelectric Point of Lecithin.

The method was to determine, by hydrogen ion concentration measurements, the degree of hydrolysis of choline chloride.

Pure choline chloride was allowed to crystallise slowly from absolute alcohol, to which a few drops of concentrated HCl had been added, at room temperature. The excessively hygroscopic needles obtained were kept in an evacuated desiccator for forty-eight hours.

The melting-point of the gold salt was 245° C. (Beilstein 244°-245° C.). The  $p_{\rm H}$  values of the solutions were measured both by the gold-quinhydrone electrode (Corran and Lewis, 1924) and by the glass electrode (Harrison, 1930).

If the original concentration of choline chloride in the solution is C moles/litre, then the dissociation constant Kb of choline is given by

$$p_{Kb} = p_{Kw} - \log_{\cdot} C - 2p_{H}.$$

That there was general agreement between the values of Kb observed at various dilutions shows that spurious effects due to the presence of free acid or base were absent (Table I.). As a further precaution, part of the choline chloride used for the above solutions was again crystallised from absolute alcohol. The value of Kb using this material agreed with the above.

The values of the dissociation constants of glycerophosphoric acid given by O. Meyerhof and J. Suranyi (1926) are as follows:

First stage dissociation constant given by  $p_{Ka_1} = 1.4$ . Second , , , ,  $p_{Ka_2} = 6.32$ .

The three dissociation constants for ortho-phosphoric acid are:

$$p_{Ka_1} = 1.96$$
;  $p_{Ka_2} = 6.7$ ;  $p_{Ka_3} = 12.4$ , (Beilstein).

It will be observed that the first and second stage constants of glycero-phosphoric acid are of the same order, respectively, as the first and second stage constants, rather than the second and third stage constants, of phosphoric acid.

It is assumed, therefore, that the dissociation constant Ka of substituted glycero-phosphoric acid (e.g., lecithin) is of the order of the first stage constant rather than the second stage constant of glycero-phosphoric acid.

The isoelectric point of lecithin, calculated from the equation: isoelectric  $p_{\rm H}=\frac{p_{Ka}-p_{Kb}+p_{Kw}}{2}$ , is given in the final column of Table I. which summarises the observed  $p_{Kb}$  values.

TABLE I.

Initial Concentration	⊅ <sub>H</sub> (Mean V	alues).		Calculated Isoelectric
(C) of Choline Chlorine, moles/litre.	Quinhydrone.	Glass.	₽Kb•	p <sub>H</sub> of Lecithin.
0.038 0.026 0.019 0.0065 0.0403	5·13 5·28 5·30 5·60 5·20	5·12 5·28 5·28 5·57 5·20	5·16 5·02 5·12 4·99 4·99	5·12 5·19 5·14 5·20 5·20

Mean value of  $p_{Kb} = 5.06$ .

Mean value of the calculated isoelectric point = 5.17.

It may be observed here that if one assumes the value of  $p_{Ka}=1\cdot 4$  for lecithin, then a value of  $Kb=4\times 10^{-11}$  is demanded for an isoelectric point (vide infra) represented by  $p_{\rm H}=2\cdot 7$ . This value for Kb, considering the nature of the basic residue of lecithin, is an unreasonably low value. This in itself points to the  $p_{\rm H}$  of net equality of charges on the zwitterions being much more towards the alkaline side than  $p_{\rm H}=2\cdot 7$ , the point of reversal of charge.

#### Extraction and Purification of Lecithin.

The lecithin was extracted from fresh egg yolks and purified by the method of Levene and Rolf (1927). The material so prepared was kept in a dark desiccator under dry nitrogen. Observations on the physico-chemical stability of the substance are given below.

Electrophoretic measurements were carried out on 0.05 per cent. dispersions but no difference was observed in the mobility if 0.025 per cent. dispersions were used. A 0.25 per cent. dispersion was prepared by shaking with water and was diluted with buffer to the requisite concentration. The ionic concentration of the buffer was the same in each case, namely 0.01N.

It was found that a dispersion from freshly prepared lecithin had a very much lower electrophoretic value (about 20 per cent. lower) than had a dispersion prepared from lecithin which had been kept in the solid state for a period of about a week in the dark under dry nitrogen. It was, in fact, found that the mobility of a freshly prepared dispersion of lecithin increased, at a given  $p_{\rm H}$  value, with the age of the lecithin used for the dispersion, during a period of about three weeks, when the mobility became constant and remained constant for at least four months at a value approximately double that observed for dispersions prepared from freshly extracted lecithin.

A number of attempts were made to reverse this behaviour but the change is apparently irreversible. The problem of the mechanism of the change is not pursued in the present work, except to observe that it cannot be a surface change since if lecithin already in the stable condition is dissolved in ether and the ether then evaporated or alternatively if the lecithin be precipitated by pouring the ethereal solution into acetone, no change in the electrophoretic mobility of the lecithin

 $<sup>^{2}\,\</sup>mathrm{I.}\,$  Y. Suyeyoshi and K. Kawai (1932) have likewise obtained evidence of an "ageing" effect in lecithin.

takes place. Further, if the final stage in the preparation of the lecithin is repeated (viz., emulsification of the lecithin with ether and 10 per cent. aqueous acetic acid and precipitation of the lecithin by pouring the emulsion into dry acetone), no change in the electrophoretic mobility from the stable condition can be observed.

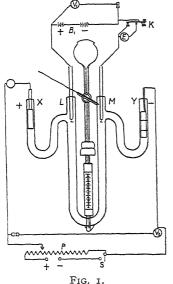
The above phenomenon may possibly be due to a lesser hydrophilic character of the freshly prepared (solid) material.

Only measurements carried out on freshly prepared dispersions of lecithin which had already attained the stable condition, are discussed in the present work.

### Experimental.

The dispersions investigated are opalescent in appearance and lend themselves excellently to a macroscopic method of observing their electrophoretic mobilities.

A diagram of the tube used for the electrophoretic mobility measurements is shown in Fig. 1. In order to minimise irregularities due to



adsorption of certain ions on a glass surface, the tube was made of quartz. The main U tube has two side arms (X.Y.) the object of which is to prevent polarisation products from migrating into the main tube. The filling arm was attached to a glass tap and funnel by a ground glass-quartz joint.

Gassing was prevented at the main electrodes in the side arms by the use of a solid zinc cylinder as anode (a device invented by Hittorf) and as cathode, a hollow lead cylinder on which PbO<sub>2</sub> was "formed." <sup>3</sup> The zinc electrode, furthermore prevented the liberation of rapidly

moving H<sup>+</sup> ions at the anode. The length of the side arms was

sufficient to prevent OH- ions, liberated at the cathode (hence also the more slowly moving Zn++ ions liberated at the anode), from migrating into the main tube; 4 thus any change in ionic concentrations and consequent change in

resistance was confined to the side arms. That this was attained was shown by the observation that there was no change in the value of the current running through the cell if the potential across L.M. was kept constant in the manner described below.

3 A number of these electrodes were "formed" in 20 per cent. H2SO4 by intermittent reversal of the current (25 milliamps.) for 3 days.

After fully charging at 20 milliamps., the capacity of an electrode, at discharging rate of 10 milliamps., was found to be 8 milliamp. hours, which was ample for the purpose.

<sup>4</sup> The potential gradient used was of the order of 2 volt/cm. The migration of OH- ions in 30 minutes (the time of duration of a "run") is 7 cm. The effective length of each side arm was 15 cm. (approximately).

The electrodes in the main tube L.M. (Fig. 1) were small platinum wires <sup>5</sup> adjusted to marks on the tube. The effective distance between the above two marks was determined by conductivity measurements.

In order to keep the potential gradient across the main tube (L.M.) constant, the potential across the side arms (X.Y.) had to be adjusted at two-minute intervals throughout the "run." The arrangement used to effect this adjustment is shown diagrammatically in Fig. 1.

A balance method was employed. A battery of accumulator cells (B.) of constant E.M.F. (this E.M.F. was measured by a high resistance

precision voltmeter V.) was used as a standard.

The E.M.F. of "B" had any convenient value and the potential across L.M. was adjusted every few minutes to be exactly equal to this standard by varying the potential across X.Y. by means of the potentiometer (P). The balance was obtained with the capillary electrometer (E). Consequently no current passed from L.M. and precise adjustment and maintenance of a constant potential gradient in the main tube were possible.

Each limb of the main tube was illuminated from the side by a separate narrow beam of intense light. In this way a vertical cross-section of both interfaces was very clearly defined. The position of each interface was measured, on the scale attached to the tube, by means of a horizontal telescope which was capable of movement in any vertical

plane.

The tube was immersed in a glass thermostat one face of which, (i.e., the face between the scale and the telescope) was ground optically plane. The movement of the boundary could be measured to within 0.25 millimeter (I-2 per cent.).

The  $p_{\rm H}$  values below  $p_{\rm H}=7$  were measured by the gold-quinhydrone electrode (Corran and Lewis). For higher values of  $p_{\rm H}$  the glass electrode

(Harrison) was used.

# The Electrophoretic Mobility of 0.05 Per Cent. Aqueous Lecithin Dispersions.

The lecithin dispersions were buffered with citrate buffer with a maximum concentration of citrate ion = 0.01N. It should be pointed out that this concentration refers to about  $p_{\rm H}=5.0$  in which region the lecithin dispersion is negatively charged. For  $p_{\rm H}$  values at which the dispersion is positively charged the concentration of citrate ion is negligible.

Powis (1915) found that while the effect on the electrophoretic velocity of a negatively charged engine oil emulsion, of a uni-univalent salt was small, at the above concentration (0·01N), the effect of a salt with a univalent cation and a multivalent anion was even less. Also in general, one would expect that the effect of a neutral salt would be less on an amphoteric body like lecithin than on an oil emulsion.

It seems justifiable, therefore, to consider the mobilities determined below to be very little removed from the absolute values.

<sup>5</sup> Calomel electrodes may be used at L.M. Platinum wire electrodes are, however, sufficiently reproducible for the purpose.

It should be noted that platinum discs act here as bipolar electrodes and considerable electrolysis takes place at the metal surfaces.

The supernatant liquid was citrate buffer of the same ionic concentration as the dispersion.<sup>6</sup> The  $p_{\rm H}$  value of the supernatant liquid agreed to within 0.01 of a  $p_H$  unit with that of the dispersion, in all cases.

It was found that the addition of 2 per cent. of sucrose to the dispersion greatly facilitated the adjustment and maintenance of a sharp boundary without affecting the mobility in any way. This is in accordance with experiments of Northrop and Cullen (1921-22).

The values of the velocities obtained in cm./sec. under a potential gradient of I volt/cm. were corrected to 20° C. by multiplying by the factor  $\eta_x/\eta_{20^{\circ}\text{C}}$ , where  $\eta_x$  and  $\eta_{20^{\circ}\text{C}}$  are respectively, the viscosities of water 7 at the temperature of measurement and at 20° C.

A representative record of an electrophoretic mobility determination is given :--

Composition of dispersion: 0.05 per cent. lecithin; 2 per cent. sucrose; N/100 citrate buffer.

$$p_{\rm H} = 5.78$$
.

Balancing P.D. across L.M. (Fig. 1): 93.0 volts. P.D. across X.Y. (Fig. 1). Initial = 160 volts; final = 164 volts. Temp. =  $19.5^{\circ}$  C. Current = 3.1 milliamps.

Movement of boundary \* (scale divisions):

Anode Limb	Cathode Limb	Time
(Upwards).	(Downwards).	(Mins.).
0·0	0·0	0
5·5	5·5	10
II·0	11·0	20
I6·0	16·5	30

Mean movement = 16.25 divisions in thirty minutes (I scale division = 0.043 cm.).

Electrophoretic velocity under a potential gradient of I volt/cm. at  $20^{\circ}$  C. =  $13.75 \times 10^{-5}$  cm./sec.

### The Electrophoretic Mobility of 0.02 Per Cent. Aqueous Dispersions of Tristearin, $\alpha\alpha'$ Dipalmitin and $\beta$ Azelao- $\alpha\alpha'$ Distearin.

In order to compare the electrophoretic behaviour of fats similar to the fatty residue of lecithin, but which do not contain an amphoteric grouping, measurements, under the same conditions as those previously described for lecithin, were carried out on dispersions of tristearin,  $\alpha\alpha'$  dipalmitin and  $\beta$  azelao- $\alpha\alpha'$  distearin. It should be pointed out that the latter fat, as distinct from the others, contains a free, ionisable carboxyl group.

6 Tiselius (1927) has shown that boundary anomalies are as small as possible when the dispersion is dilute with respect to the dispersing phase and both the dispersion and the supernatant liquid contain the same electrolytes in quantity

to give practically the same conductivity.
The change in viscosity due to the addition of 2 per cent. sucrose is negligible and the ratio  $\eta_s/\eta_{20}$ °C., for the solutions used, is not sensibly different from that of water at the same temperature.

\* Note: The position of each interface was observed every ten minutes.

These intermediate values are recorded in order to give assurance that the rate of movement was uniform and no numerical use is made of them.

TABLE II.—Showing the Variation of Electrophoretic Mobility with  $p_{\rm H}$  Values using 0-05 per cent. Aqueous Dispersions of Lecithin.

1	The	sign	denotes	the	sign	of	the	charge).
١	, 1110	Sign	denotes.	cnc	31811	O1	unc	charge,

p <sub>H</sub> Values.	Electrophoretic Mobility under a Potential Gradient of 1 volt/cm. at 20° C. cms./sec.	⊅ <sub>H</sub> Values.	Electrophoretic Mobility under a Potential Gradient of 1 volt/cm. at 20° C. cms./sec.
10·33 9·90 8·14 7·31 6·70 6·57 6·26 6·00 5·93 5·78 5·64 5·60	- 30.4 × 10 <sup>-5</sup> - 29.8 - 29.75 - 24.9 - 19.6 - 19.3 - 16.7 - 14.5 - 14.25 - 13.75 - 12.3 - 12.0	5.54 5.34 4.84 4.61 4.35 3.80 3.50 2.95 2.75 2.45 2.28 2.20	- 11.6 × 10 <sup>-5</sup> - 10.35 - 8.8 - 8.6 - 8.15 - 6.7 - 5.1 - 3.5 - 0.4 + 10.5 × 10 <sup>-5</sup> + 15.6 + 17.1

The curve plotted from these values will be discussed later (Fig. 2).

The fats in question were prepared in the Department of Applied Chemistry of the University of Liverpool and were of a high degree of purity.

For the sake of comparison the accepted structures of lecithin and the above fats may be written down:—

Lecithin. ("R" represents a mixture of unsaturated fatty acid residues as well as stearic and palmitic.)

Tristearin.

#### (a) Tristearin.

0.5 gm. of tristearin dissolved in 10 c.c. of hot alcohol was poured slowly with continual shaking, into 1 litre of water at  $73^{\circ}$  C. (just above the melting-point of the fat), and the shaking was continued for ten minutes. The dispersion was then left overnight and filtered. The concentration of tristearin in the dispersion was 0.02 per cent.

In appearance the dispersion resembled a dispersion of lecithin and the same apparatus and method was used to determine its electrophoretic mobility at various  $p_H$  values.

TABLE III. - Showing the Variation OF ELECTROPHORETIC MOBILITY WITH ψ<sub>H</sub> VALUES, USING 0.02 PER CENT. DISPERSIONS OF TRISTEARIN.

(The sign denotes the sign of the charge.)

TABLE IV. - Showing the Variation OF ELECTROPHORETIC MOBILITY WITH  $p_{\rm H}$  Values, using 0.02 per cent. Dispersions of  $\alpha\alpha'$  Dipalmitin.

(The sign denotes the sign of the charge.)

₽ <sub>H</sub> -Values.	Electrophoretic Mobility under a Potential Gradient of I Volt/cm. at 20° C. Cms./sec.
7·16	- 40.5 × 10 -5
6·82	- 36.2
6·05	- 25.7
5·57	- 20.4
4·84	- 16.1
4·08	- 14.2
3·06	- 11.1
2·41	- 3.4
2·00	0.0 (immediate flocculation)

# (b) $\alpha\alpha'$ Dipalmitin.

Dispersions of  $\alpha\alpha'$  dipalmitin were prepared in a similar manner to those of tristearin. No change in electrophoretic mobility was observed if the method of preparation was varied slightly, (i.e., if the

$p_{ m H}$ Values.	Electrophoretic Mobility under a Potential Gradient of I volt/cm. at 20° C. cms./sec.
6.84 6.18 6.06 5.61 4.97 4.95 4.92 4.60 4.53 4.07 4.05 3.49 3.13 2.73 2.42 2.00	- 39.4 × 10 <sup>-5</sup> - 30.9 - 30.9 - 25.3 - 20.8 - 20.4 - 19.3 - 18.9 - 18.2 - 18.1 - 16.2 - 13.6 - 10.4 - 5.6 - 0.0 (immediate flocculation)

(No reversal of the sign of the charge was obtained.)

temperature or the quantity of fat used was varied). The concentration of the dispersion, in each case, was 0.02 per cent. (approximately).

TABLE V .- Showing the Variation of Electrophoretic Mobility with  $p_{\rm H}$  Values, using 0.02 per cent. Dispersions of  $\beta$  Azelao- $\alpha\alpha'$  Distearin.

(The sign denotes the sign of the charge.)

⊅ <sub>H</sub> Values.	Electrophoretic Mobility under a Potential Gradient of x volt/cm. at 20° C. cms./sec.		
8.92 7.02 6.41 6.01 5.78 5.61 5.43 5.07 4.97 4.86 4.70 4.55 4.20 3.20	- 43.9 × 10 <sup>-5</sup> - 42.3 - 40.1 - 36.9 - 33.2 - 31.0 - 27.7 - 26.6 - (Complete f	locculation.) ,, ,, ,,	

The values given in Tables II. to V. are plotted in Fig. 2.

The electrophoretic mobility  $-p_{\rm H}$  curve was determined in the same manner as the corresponding tristearin curve.

# (c) $\beta$ Azelao- $\alpha\alpha'$ Distearin.

Dispersions of this substance were prepared, and its electrophoretic mobility determined, in a similar manner to that used for tristearin and aa' dipalmitin dispersions.

#### Discussion.

From the electrophoretic mobility  $-p_{\rm H}$  curves (Fig. 2), it will be observed that the point of reversal of the sign of the charge on a lecithin dispersion corresponds to  $p_{\rm H}=2.7$ . This value confirms the value

of the effective 8 isoelectric point found by Fugii and by Price and Lewis. As already pointed out this value does not correspond to the true 8 isoelectric point.

In order to explain the discrepancy between the effective and the true isoelectric points it is postulated that the charge on a lecithin dispersion is a composite term, being made up of the charge due to dissociation of the amphoteric grouping and that due to adsorption of, presumably, hydroxyl ions on the fatty surfaces of the particles.

A similar type of phenomenon has

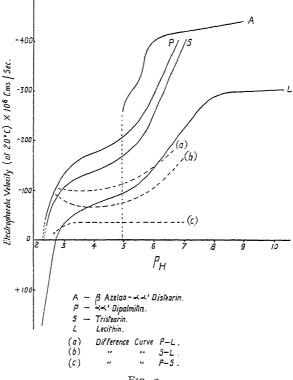


FIG. 2.

already been met with by H. R. Kruyt and J. J. Went (1931), who point out that it might be expected that dispersions of certain amino compounds (e.g.,  $\beta$ -naphthylamine) would have a positive charge. These compounds, however, are found to have a negative charge. The hydrocarbons themselves (e.g, naphthalene) have a negative charge and it would appear improbable that, in general, one amino group in the

<sup>8</sup> The point at which actual reversal of the sign of the charge takes place is referred to as the effective isoelectric point and the point of net equality of the charges on the zwitterions from the amphoteric groupings as the true isoelectric point.

molecule should be able to reverse the charge at the surface. Nevertheless, the presence of amino groups does appear to reduce, to a large

extent, the value of the negative charge.

If we regard lecithin as an amphoteric body with an additional charge due to adsorption of hydroxyl ions on the surface, it will follow that the *effective* isoelectric point will correspond, not to the  $p_{\rm H}$  at which the positive and negative charges on the zwitterions are equal, as usually assumed in the case of proteins, but to a point further removed towards the acid region, at which the positive charge due to dissociation is sufficiently great to be equal to the resultant negative charge. This is in accordance with the discrepancy between the calculated and the observed isoelectric points.

We are led by the above considerations to inquire into the relation-

ship of the two components to the resultant charge.

From the electrophoretic mobility  $-p_{\rm H}$  curves for tristearin and dipalmitin dispersions and the difference curves deduced therefrom, we obtain some knowledge of the behaviour of a fat representative of lecithin without its amphoteric groupings, *i.e.*, a hypothetical body

owing its charge simply to adsorption of hydroxyl ions.

Although a dipalmitin dispersion has a greater charge than a tristearin dispersion, under the same conditions, the difference curve, at least for the range  $p_{\rm H}=3$  to  $p_{\rm H}=7$  representing a change in hydrogen ion concentration of 10<sup>4</sup> times, is horizontal (Fig. 2). That is, the rate of change of mobility with  $p_{\rm H}$  is the same in each case. A further simple relationship between the mobilities of tristearin and dipalmitin will be discussed later.

It is assumed, therefore, that the mobility  $-p_{\rm H}$  curve of the hypothetical simple fat from lecithin, referred to above, also bears a constant

difference relationship to the corresponding dipalmitin curve.

With this assumption we may attempt to predict the shape of the difference curve between the respective mobility —  $p_{\rm H}$  curves of dipalmitin and lecithin. It will be recalled that the lecithin curve lies below that for dipalmitin.

Above  $p_{\rm H}=5\cdot2$ , the *true* isoelectric point, we may look upon both the charge due to adsorption and that due to ionisation as increasing with  $p_{\rm H}$ . Consequently, if the charges from the two sources are simply additive and independent of one another, the charge on a lecithin dispersion should increase more rapidly with  $p_{\rm H}$  than the charge on a dipalmitin dispersion, over the corresponding range of  $p_{\rm H}$  values, *i.e.*, the difference curve between the respective dipalmitin and lecithin mobility  $-p_{\rm H}$  curves should diminish with increasing  $p_{\rm H}$  (Fig. 2). Similarly below  $p_{\rm H}=5\cdot2$ , under which condition the lecithin amphoteric grouping exhibits a positive charge, the difference curve should rise.

The results obtained (Fig. 2), however, contradict this and above  $p_{\rm H}=5.2$ , the difference curve in question rises with increasing  $p_{\rm H}$ .

The simple assumption that the charge due to adsorption of hydroxyl ions on the surfaces of particles of a lecithin dispersion and the charge due to ionisation of the particles are independent and additive appears, therefore, not to be valid and the presence of the amphoteric groups fundamentally influences the adsorption charge.

The same conclusion may be arrived at in a different manner which, incidentally, brings out an interesting  $p_{\rm H}$  — mobility relationship for the fats under consideration.

If the electrophoretic mobility of tristearin or dipalmitin is plotted

against the reciprocal of the cube root of the hydrogen ion concentration,  $I/\sqrt[3]{[H^+]}$ , a straight line results in each case (Fig. 3) for the range  $p_{\rm H}=3.5$  to  $p_{\rm H}=7$ ; *i.e.*, the mobility is a linear function of  $I/\sqrt[3]{[H^+]}$ . Moreover, the curves obtained in this way for dipalmitin and tristearin are parallel (Fig. 3).9

We may assume that the corresponding curve for the hypothetical fat, representing the fatty part of the lecithin molecule without its amphoteric groups, would also be parallel to the tristearin or dipalmitin curves. Further, at a value of  $I/\sqrt[3]{[H^+]}$  represented by  $p_H = 5.2$  (the point of net equality of charges on the zwitterions of lecithin)

the mobility of the above "hypothetical fat" should be identical with that observed for lecithin itself. A curve representing the "hypothetical fat" mobility

$$- I/\sqrt[3]{[H^+]}$$

relationship obtained from these data is shown (Fig. 3) as a dotted line

It is at once evident (Fig. 3) that the above "hypothetical fat" mobility

$$- I/\sqrt[3]{[H^+]}$$

curve cuts the corresponding curve for lecithin itself, in a direction contrary to that which would be followed if the two sources of charge were in-

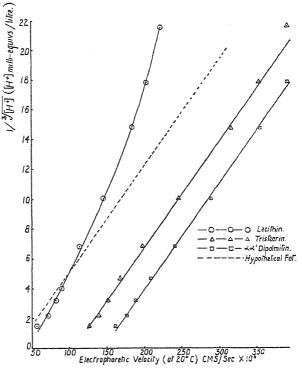


Fig. 3.

dependent and additive. That is, above the point of intersection, corresponding to the *true* isoelectric point of lecithin, the charge on a body exactly representative of the fatty part of lecithin alone is actually greater, for a given hydrogen ion concentration, than that on lecithin as a whole, in spite of the fact that the ionisation charge has the same sign as the adsorption charge. We are, therefore, again led to the conclusion that the presence of the amphoteric grouping has a fundamental influence upon the adsorption charge of a lecithin dispersion.

The result of this influence is, in the first place, to lower the initial

<sup>&</sup>lt;sup>9</sup> Other functions of H<sup>+</sup> of the type  $(H^+)^{-\frac{1}{x}}$  do not give even approximate straight lines when plotted against the mobility.

value of the charge on a lecithin dispersion and again effectively to decrease the rate of discharge by hydrogen ions, to values even less than those which would obtain if the negative charge due to ionisation were entirely absent.

A possible mechanism for this influence is as follows. the  $p_{\rm H}=6.8$ , which corresponds to the hydrogen ion concentration during the formation of the dispersion in the absence of a buffer. At this  $p_{\rm H}$  the ionisable groupings give the particles a negative charge. It is conceivable that this negative charge repels hydroxyl ions from the purely fatty portion of the surfaces of the particles. Consequently, the particles as a whole may not adsorb hydroxyl ions to the same extent as a simple fat would do. Thus, when we consider the discharging effect of hydrogen ions, above  $p_{\rm H}=5.2$ , we are dealing to a large extent with the "throwing back" of the ionisation of the amphoteric groupings and only to a minor extent (compared with tristearin) with the adsorption charge at the surface. In such a case, the discharging effect due to a given increase of hydrogen ion concentration, in this region, might well be less than that produced by a corresponding increase of hydrogen ion concentration in the case of a simple fat representing the fatty residue of lecithin.

In the case of a lecithin dispersion below  $p_{\rm H}=5\cdot2$  the positive charge from the ionised groupings will increase with fall in  $p_{\rm H}$ , while the negative charge due to adsorption will decrease. If the discharging efficiency of the hydrogen ions were the same in this case as in tristearin, we might expect that the net negative charge on the surface would decrease much more rapidly than that of tristearin. It will be observed, however, (Fig. 2) that below  $p_{\rm H}=5\cdot2$ , the slope of the lecithin curve is very similar to that for tristearin. This suggests that the presence of the positively charged ionised groupings tend to repel hydrogen ions and consequently to decrease their discharging efficiency upon the fatty portion of the surface.

The profound effect of a free ionisable group on the charge of a fatty body is shown strikingly by a comparison of the mobility —  $p_{\rm H}$  curves for tristearin and for  $\beta$  azelao- $\alpha\alpha'$  distearin. In fact, from the extremely rapid fall in charge with decrease in  $p_{\rm H}$  value and the ultimate complete discharge at as high a value as  $p_{\rm H}=4\cdot 8$ , it would appear that in this case the adsorption charge is of minor importance.

Returning to the consideration of lecithin as an amphoteric body, it would appear from the foregoing discussion that although the negative charge arising from ionisation at  $p_{\rm H}=5\cdot 2$  is supplemented by a negative charge from adsorption on the surface, the magnitude of the adsorption charge, and consequently the part played by this charge in the resultant charge, is very much less than that which one would associate with a fatty surface of the size and type possessed by lecithin.

#### Summary.

I. The dissociation constant of choline has been determined, viz.,  $p_{Kb} = 5.06$ . The isoelectric point of lecithin, from approximate values of its dissociation constants, is calculated to be at  $p_{\rm H} = 5.2$ .

2. The physico-chemical stability of pure egg lecithin, prepared by the method of Levene and Rolf, in the dry solid state, has been briefly investigated. It is shown that an ageing effect is present.

3. A satisfactory method of controlling the potential gradient in an electrophoresis tube has been described.

4. The electrophoretic behaviour of lecithin has been studied and the point of reversal of charge found to correspond to the value of the isoelectric point found by Fugii and by Price and Lewis, namely  $p_{\rm H}=2.7$ .

5. It is suggested that the discrepancy between the observed and the calculated isoelectric points of lecithin is due to the complex nature of the charge, part of it being due to ionisation and part to adsorption.

6. The electrophoretic behaviour of aqueous dispersions of tristearin,

 $\alpha\alpha'$  dipalmitin,  $\beta$  azelao- $\alpha\alpha'$  distearin has also been studied.

7. A simple difference relationship between the mobility  $-p_{\rm H}$  curves

of tristearin and  $\alpha\alpha'$  dipalmitin dispersions has been noted. 8. It has been found that the mobility of both tristearin and  $\alpha\alpha'$ dipalmitin is a linear function  $1/\sqrt[3]{[H^+]}$ , for the range  $p_H = 3.5$  to  $p_H = 7$ . And further, that the mobility  $-1/\sqrt[3]{[H^+]}$  curves for dispersions of these

two fats are parallel.

9. From a comparison of the electrophoretic behaviour of lecithin and of the simple fats investigated, the conclusion has been arrived at that although the negative charge due to ionisation at  $p_{\rm H} > 5.2$  is supplemented by an adsorption charge, the influence of the adsorption charge is much less than that which would be expected from a fatty residue of the type possessed by lecithin.

10. A possible mechanism for the influence of the ionisation charge

upon the adsorption charge has been given.

The authors desire to express their indebtedness to Imperial Chemical Industries Ltd. for a grant to the Department of Physical Chemistry of the University of Liverpool.

Our best thanks also are due to Professor T. P. Hilditch of the University of Liverpool for a gift of samples of the fats (other than lecithin) used in the foregoing work.

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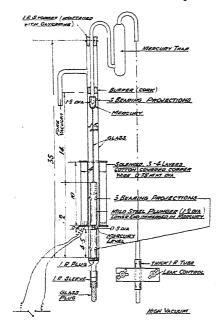
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# A PRESSURE REGULATOR FOR GAS-FILLED X-RAY TUBES.

By F. D. MILES.

Received 4th May, 1933.

The demountable gas-filled tubes for work in X-ray analysis, of which the Shearer and Hadding types are the best known and most widely used, have considerable stability when in correct adjustment, but any tube of this kind, nevertheless, requires attention from time to time to counteract variations in the pressure of the gas. Several arrange-



PRESSURE REGULATOR FOR SHEARER X RAY TUBE

(DIMENSIONS IN CM)

ments by which the control may be rendered automatic have already been described 1 and there might appear to be a little need for another. The device of which details are given in this note, however, is very simple to make, reliable, and specially suitable for insertion in the usual gascircuit of the Shearer tube. The variations in the primary current of the transformer are utilised to open and close the bye-pass between the high and fore vacua, and no attempt is made, as in arrangements which have been proposed previously, to control the passage of gas through the main connection between the tube and the pumps, The method of controlling the bye-pass connection has considerable advantages.

The body of the regulator consists of a glass tube about 35 cm. long and of about 15 mm. bore. In this, works smoothly up and down an armature made

from a piece of soft iron rod  $\frac{1}{2}$  inch in diameter. The lower end of this is immersed in mercury which, when the armature is in its lowest position, reaches nearly to the top of the waist which has been turned out to make the effective weight less dependent on the extent of submergence. Bearing points are formed by making three sloping saw-cuts at top and bottom and bending outwards the tapering fins of metal which result. The small quantity of mercury required to close the end of the tube leading to the high vacuum is contained

 $<sup>^{1}</sup>$  Bozorth, J. Am. C. S., 49, 971, 1927; Haworth, J.O.S.A., 19, 79, 1929; White, J. Sci. Inst., 7, 99, 1930.

in a glass cup which is kept central in the tube by three sealed-on glass projections. In order to avoid volatilisation of the mercury, this cup is sealed to a glass rod about 12 cm. long, the lower end of which rests in a hole drilled in the head of the armature. An india-rubber plug, with a notch cut in the edge for the mercury to pass, acts as the lower buffer and an ordinary cork, sealed on to the gas lead and making a loose sliding fit with the tube, acts as the upper one.

The solenoid is wound on a former 10 cm. long, which can be pushed up and down over the tube and fixed with a clip. For the length given, from three to four layers of No. 21 cotton-covered copper wire are sufficient when the primary transformer current is 4 amps. but the most effective amount of wire is best fixed by trial. Thinner wire than this

should not be used.

The usual controllable leak is necessary, in series with the regulator. It is difficult to find anything better than the ordinary form in which a metal plate can be screwed down across a thick piece of rubber vacuum tubing. A switch should also be arranged to short-circuit the solenoid of the regulator at will.

In operating it is convenient to start the tube with the regulator short-circuited and to adjust the leak so that the current through the tube, as shown by a milliameter, is very slowly increasing. The regulator is then switched in and the solenoid is moved down the glass tube until the armature rises and the pressure in the X-ray tube falls. When the milliamperage has fallen to the desired figure the solenoid is raised until the armature just falls and is then clipped in position.

The sensitiveness of the arrangement to alteration of voltage is greater than is usually required. In practice the extent of the variation in the tube current when the regulator is in control depends on the pressure in the fore-vacuum and the rate of passage through the variable leak. The setting in which the variation is about 10 per cent. is easily obtained and is very satisfactory in working. Adjusted to this degree the whole apparatus can be left all day without attention.

I wish to acknowledge the permission accorded by Messrs. Imperial Chemical Industries Limited for the publication of this note.

The Nobel Laboratories, Ardeer.

# A THEORY OF THE RATE OF SOLUTION OF SOLID INTO LIQUID.

By Susumu Miyamoto.

Received 8th May, 1933.

The rate of solution of solid into liquid 1 is generally expressed by

$$\frac{\mathrm{d}c}{\mathrm{d}t} = KS(c_{\infty} - c) \qquad . \tag{1}$$

where c is the concentration of the dissolved substance in the liquid

<sup>1</sup> Noyes and Whitney, Z. physik. Chem., 23, 689, 1897; Nernst, Z. physik. Chem., 47, 52, 1904; Brunner, Z. physik. Chem., 47, 56, 1904.

phase,  $c_{\infty}$  the saturation concentration, S the area of the boundary surface, and K a constant.

Noyes, Whitney and Nernst proposed that equation (I) represents the rate of diffusion by assuming that a film of saturated solution is continuously present on the surface of the solid phase, and that a diffusion layer of proper thickness is present at the interface. The thickness of the diffusion layer is from about  $2 \times 10^{-3}$  to  $5 \times 10^{-3}$  cm. according to this diffusion layer theory.2

The rate of solution of metals or metallic oxides into acidic solution is expressed by

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -KSc \quad . \qquad . \qquad . \qquad . \qquad (1')$$

where c is the concentration of the acid. This equation is similarly derived by assuming that the rate of solution is the rate of diffusion of the reacting substance through the diffusion layer.

It is difficult to interpret many experimentally obtained facts by this

diffusion layer theory. For example,

- (a) The rates of solution of metals into acidic solution are independent of the rate of stirring when the velocity of stirring is sufficiently high.3
  - (b) The rates of solution of the different faces of a crystal are different.4
- (c) The rate of solution is dependent on the curvature of the solid surface.5
- (d) Roller studied the rates of solution and the size of the solid particles, and concluded that no diffusion layer exists at the boundary surface.6

Theories of the rate of solution of solid into liquid, which do not assume the existence of a diffusion layer, were proposed by several

A new theory of the rate of solution of solid into liquid, similar to the theory 8 of the rate of solution of gas into liquid, which had been proposed by the present writer based upon the kinetic theory of gases, is given in the following.

# A New Theory of the Rate of Solution of a Solid into a Liquid.

The process of solution of a solid into a liquid can be separated into two processes, namely the escape of the solid molecules into the liquid phase and the deposition of the dissolved molecules on the solid surface. Then the rate of solution of the solid into the liquid can generally be given by

$$\frac{N}{S} \left( \frac{\mathrm{d}n}{\mathrm{d}t} \right) = N_1 - N_2 \quad . \tag{2}$$

<sup>2</sup> Brunner, loc. cit.; Wagner, Z. physik. Chem., 71, 401, 1910. <sup>3</sup> Centnerszwer and Zablocki, Z. physik. Chem., 122, 455, 1926; Centnerszwer and Straumanis, ibid., 128, 369, 1927; Centnerszwer, ibid., 137, 352, 1928;

141A, 297, 1929.

4 Tammann and Sartorius, Z. anorg. Chem., 175, 197, 1929; Glauner, Z. physik. Chem., 142, 67, 1929.
5 Luce, Ann. Physique, 11, 167, 1929.

<sup>6</sup> Roller, J. Physic. Chem., 35, 1133, 1931; 36, 1202, 1932.

<sup>7</sup> Ericson-Auren, Z. anorg. Chem., 18, 83, 1898; 27, 209, 1901; Palmaer, Z. physik. Chem., 56, 689, 1906; Wildermann, Z. physik. Chem., 66, 445, 1909.

<sup>8</sup> Miyamoto, Chem. News, 144, 273, 1932; Bull. Chem. Soc. Japan, 7, 8, 388, 1932.

where N is Avagadro's constant, S the area of the boundary surface,  $N_1$  the number of molecules of the solid which enter the liquid phase per unit area of the interface per unit of time,  $N_2$  the number of molecules which deposit per unit area of the interface per unit of time, n the number of moles of the dissolved substance in the liquid phase.

According to Maxwell's distribution law, the number of molecules whose component of the energy of vibration at right angles to a fixed plane lies between  $\epsilon$  and  $\epsilon+d\epsilon$  among N' molecules is given by

$$dN = \frac{N'}{kT} e^{-\frac{\epsilon}{kT}} d\epsilon . (3)$$

where k is Boltzmann's constant.

If it is assumed that among the molecules which make up the surface of the solid, only those, whose components of the energy of vibration at right angles to the interface are greater than a threshold value  $\epsilon_0$ , are able to enter into the liquid phase, then

$$N_1 = \frac{N_0}{kT} \int_{\epsilon_0}^{\infty} e^{-\frac{\epsilon}{kT}} d\epsilon = N_0 e^{-\frac{\epsilon_0}{kT}} = N_0 e^{-\frac{N\epsilon_0}{RT}} . \tag{4}$$

where  $N_{\rm 0}$  is the number of molecules which make up unit area of the solid surface.

According to the assumption above mentioned it is easily seen that the value  $\epsilon_0$  depends upon the relative nature of solid and liquid, temperature, pressure and the packing of molecules in the solid surface. The value  $N_1$  increases or decreases as the value  $\epsilon_0$  decreases or increases.

The value  $N_2$  is obtained in the following way.

By Maxwell's distribution law of velocities,

$$dN = \frac{N^{\prime\prime}}{\sqrt{\frac{2\pi RT}{M}}} e^{-\frac{Mu^2}{2RT}} du \qquad (5)$$

where dN signifies the number of molecules whose components of velocities at right angles to a fixed plane lie between u and u+du among N'' molecules in the liquid phase, M the molecular weight of the dissolved substance, R the gas constant, and T the absolute temperature.

Now a further assumption is made. Among the molecules which collide with the solid surface, only those whose components of velocities at right angles to the interface are greater than a threshold value  $u_0$ , are able to deposit on the solid surface. The kinetic energy of the colliding molecule will be transferred to the molecule in the solid surface at the instant of collision.

Then the value  $N_2$  is given by

$$N_2 = \int_{u_0}^{\infty} \frac{cN}{\sqrt{\frac{2\pi RT}{M}}} u e^{-\frac{Mu^2}{2RT}} du = cN \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}}.$$
 (6)

where c is the concentration of the dissolved substance expressed in moles per c.c.

The value  $u_0$  depends upon the nature of the solid and the liquid and on temperature and pressure, and the value  $N_2$  increases or decreases as the value  $u_0$  decreases or increases.

From equations (2), (4) and (6)

$$\frac{\mathrm{d}n}{\mathrm{d}t} = S\left(\frac{N_0}{N}e^{-\frac{N\epsilon_0}{RT}} - c\sqrt{\frac{RT}{2\pi M}}e^{-\frac{Mu_0^2}{2RT}}\right) . \qquad (7)$$

In the state of saturation,

$$\frac{\mathrm{d}n}{\mathrm{d}t} = 0 \qquad . \tag{8}$$

From equations (7) and (8) it follows that

$$\frac{N_0}{N}e^{-\frac{N_{e_0}}{RT}} - c_{\infty}\sqrt{\frac{RT}{2\pi M}}e^{-\frac{Mu_0^2}{2RT}} = 0 \qquad . \tag{9}$$

where  $c_{\infty}$  is the concentration of the saturated solution.

From equations (7) and (9) therefore

$$\frac{\mathrm{d}n}{\mathrm{d}t} = S\sqrt{\frac{RT}{2\pi M}}e^{-\frac{Mu_0^2}{2RT}}(c_{\infty} - c) \qquad . \tag{10}$$

Now

$$c = \frac{n}{v}, \qquad . \qquad . \qquad . \qquad (11)$$

where v is the volume of the liquid phase.

Then 
$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\mathrm{I}}{v} \frac{\mathrm{d}n}{\mathrm{d}t} = \frac{S}{v} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} (c_{\infty} - c) \qquad . \tag{12}$$

or 
$$\frac{\mathrm{d}c}{\mathrm{d}t} = KS(c_{\infty} - c) \quad . \quad . \quad . \quad (13)$$

where 
$$K = \frac{I}{v} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} . \qquad (14)$$

Thus equation (I) is derived from the new theory without assuming the existence of a diffusion layer.

Equation (I)' is similarly derived in the following way.

It is assumed that among the molecules which collide with the solid surface, only those whose components of velocities at right angles to the interface are greater than a threshold value  $u_0$ , can react with the solid.

Then from equation (6) the rate of solution is expressed by

$$-\frac{N}{S}\frac{\mathrm{d}n}{\mathrm{d}t} = cN\sqrt{\frac{RT}{2\pi M}}e^{-\frac{Mu_0^2}{2RT}} \quad . \tag{15}$$

where n is the number of moles of the reacting substance and c its concentration.

Now 
$$c = \frac{n}{v}$$
 . . . (16)

where v is the volume of the liquid.

From equations (15) and (16)

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\frac{c}{v} S \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \qquad . \tag{17}$$

or 
$$\frac{\mathrm{d}c}{\mathrm{d}t} = -KSc \qquad . \qquad . \qquad . \qquad . \tag{18}$$

where 
$$K = \frac{I}{2} \sqrt{\frac{RT}{2\pi M}} e^{-\frac{Mu_0^2}{2RT}} \qquad . \tag{19}$$

Thus equation (I)' is also derived.

The Solubility of a Solid.—From equation (9) the solubility of a solid is given by

$$c_{\infty} = \frac{N_0}{N} \sqrt{\frac{2\pi M}{RT}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2}\right)} \quad . \tag{20}$$

The solubility of a solid is dependent not only on the value  $\epsilon_0$  but on the value  $u_0$ .

#### Discussion.

Since equations (I) and (I') can be established by this theory, it is obvious that this new theory can interpret those experimentally obtained facts which were interpreted by the diffusion layer theory. It will be unnecessary to mention that equations (7) and (17) are derived similarly when the bulk of the liquid phase is quiescent and the existence of diffusion layer should be taken into consideration.

From equations (7) and (17), the rate of solution is dependent upon the values  $\epsilon_0$  and  $u_0$ . The difference 4 in the rates of solution of the different faces of a crystal is interpreted according to the present theory, as the values  $\epsilon_0$  and  $u_0$  are dependent not only on the chemical natures of the solid and the liquid but also on the packing of molecules in the solid surface.

The results of Roller's investigations 6 are similarly interpreted by equation (7).

The solubility of a solid depends upon the curvature of the solid surface.

- (a) Hulett 9 found that the solubility of gypsum increases when the size of the particle is less than  $2 \times 10^{-4}$  cm.
- (b) Dundon and Mack 10 observed an increase in the solubility of gypsum between  $0.2 \times 10^{-4} \sim 0.5 \times 10^{-4}$  cm. in size, and Dundon 11 extended these observations to other powders.

These facts are easily interpreted by equation (20).

Roller concluded from the results of his study that no theoretical Nernst film exists at the boundary surface. 12 The present writer is of the opinion that no diffusion layer of such thickness as that required by the diffusion layer theory exists at the interface of different phases when the bulk of the phases are stirred well.

Langmuir has shown that no diffusion layer exists at the interface of a gas and a solid. 13

#### Summary.

(1) A theory of the rate of solution of a solid into a liquid is proposed, based on the assumptions that among the molecules, which make up the solid surface, only those, whose components of energy of vibration at right angles to the interface are greater than a threshold value  $\epsilon_0$ , can enter into the liquid phase, and that among the molecules in the liquid phase, only those, which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value  $u_0$ , can deposit on the solid surface.

<sup>&</sup>lt;sup>9</sup> Z. physik. Chem., **37**, 385, 1901; **47**, 357, **19**04. <sup>10</sup> J. Amer. Chem. Soc., **45**, 2479, 1923. <sup>12</sup> J. Physic. Chem., **36**, 1226, 1932. <sup>13</sup> Trans. Faraday Soc., **17**, 621, 1921.

The values  $\epsilon_0$  and  $N_0$  in equation (13) depend upon the specific nature of the solid and the rate of evaporation increases or decreases as the value  $\epsilon_0$  decreases or increases.

If the rate of condensation is now considered, and it is assumed that among the molecules of the gas, which collide with the solid surface, only those, whose components of velocities at right angles to the interface are greater than a threshold value  $u_0$ , are able to condense on the solid surface, then the following equation is obtained readily from Maxwell's distribution law, as mentioned in the previous paper,7

$$N_2 = \frac{Np}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \qquad . \tag{14}$$

From equations (3) and (14) it can be shown that

$$\alpha = e^{-\frac{Mu_0^2}{2RT}} \quad . \quad . \quad . \quad (15)$$

As above mentioned the value  $\alpha$  is unity in many cases and it follows from equation (15) that the value  $u_0$  is zero in such cases. From equations (10), (13) and (14)

$$\frac{\mathrm{d}n}{\mathrm{d}t} = S\left(\frac{aN_0}{N}e^{-\frac{N\epsilon_0}{RT}} - \frac{p}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}}\right) \quad . \tag{16}$$

Equation (16) represents the rate of sublimation according to the present theory.

In the state of equilibrium,

$$\frac{\mathrm{d}n}{\mathrm{d}t}=0,$$

and from equation (16),

$$\frac{aN_0}{N}e^{-\frac{Ne_0}{RT}} = \frac{p_\infty}{\sqrt{2\pi MRT}}e^{-\frac{Mu_0^2}{2RT}} \quad . \tag{17}$$

From equations (16) and (17) it follows that

$$\frac{\mathrm{d}n}{\mathrm{d}t} = KS(p_{\infty} - p) \quad . \tag{18}$$

where

$$K = \frac{I}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} . (19)$$

Equation (18) is analogous to equation (6).

It follows from equation (16) that the rate of sublimation depends upon the curvature of the solid surface, as the value  $\epsilon_0$  according to the present theory will have a smaller value when the solid surface is convex.

#### The Initial Rate of Sublimation.

The initial rate of sublimation or the rate of sublimation in vacuo is expressed by putting p = 0 in equation (16).

$$\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_{\mathrm{Initial}} = S \cdot a \cdot \frac{N_0}{N} e^{-\frac{N_{e_0}}{RT}} \quad . \tag{20}$$

OI

$$\log \left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_{\mathrm{Initial}} = -\frac{N\epsilon_0}{2\cdot303RT} + \log \frac{S \cdot a \cdot N_0}{N} \qquad . \tag{20'}$$

From equations (17) and (20)

$$\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right)_{\mathrm{Initial}} = \frac{p_{\infty}S}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} . \qquad (21)$$

### The Vapour Pressure of a Solid.

From equation (17) the vapour pressure of a solid is expressed by

$$p_{\infty} = \frac{a \cdot N_0}{N} (2\pi MR)^{\frac{1}{2}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2}\right)} \qquad . \tag{22}$$

or

$$\log p_{\infty} = -\frac{Q}{2 \cdot 303RT} + \frac{1}{2} \log T + C \qquad . \qquad . \qquad (227)$$

where

$$Q = N\epsilon_0 - \frac{Mu_0^2}{2},$$

and

$$C = \log \frac{aN_0\sqrt{2\pi MR}}{N}.$$

From equation (22) it follows that the vapour pressure of a convex surface is greater than that of plane surface, as the value  $\epsilon_0$  according to the present theory will have smaller value in the former case.

Now the value  $N_0$ , the number of molecules which make up unit area of the solid surface, is given by

$$N_0 = \gamma \left(\frac{N}{v_m}\right)^{\frac{2}{3}} = \gamma \left(\frac{\rho N}{M}\right)^{\frac{2}{3}} \qquad . \qquad . \qquad (23)$$

where N is Avagadro's constant,  $v_m$  the molar volume,  $\rho$  the density of the solid, M the molecular weight, and  $\gamma$  a constant, the value of which depends upon the arrangement of the molecules of solid.

From equations (22) and (23) therefore

$$p_{\infty} = a\gamma N^{-\frac{1}{3}} (2\pi R)^{\frac{1}{2}} \rho^{\frac{2}{3}} M^{-\frac{1}{6}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2}\right)} \qquad (24)$$

Thus an equation analogous to equation (9) is obtained according to the present theory.

The present theory is expected to be applicable to the phenomenon of adsorption.

#### Summary.

A theory of the rate of sublimation is proposed, based upon the assumptions, that among the molecules, which make up the solid surface, only those, whose energies of vibrations at right angles to the interface are greater than a threshold value  $\epsilon_0$  can escape from the solid phase, and that among the molecules in the gas phase, only those, which collide with the interface with velocities, whose components at right angles to the interface are greater than a threshold value  $u_0$ , can condense on the solid surface.

According to this theory the rate of sublimation and the vapour pressure of solid are given by the following equations:—

$$\begin{split} \frac{\mathrm{d}n}{\mathrm{d}t} &= S \Big( \frac{aN_0}{N} e^{-\frac{N\epsilon_0}{RT}} - \frac{p}{\sqrt{2\pi MRT}} e^{-\frac{Mu_0^2}{2RT}} \Big), \\ p_\infty &= \frac{aN_0}{N} (2\pi MR)^{\frac{1}{2}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2}\right)} \end{split}$$

or

$$p_{\infty} = a\gamma N^{-\frac{1}{8}} (2\pi R)^{\frac{1}{2}} \rho^{\frac{2}{8}} M^{-\frac{1}{8}} T^{\frac{1}{2}} e^{-\frac{1}{RT} \left(N\epsilon_0 - \frac{Mu_0^2}{2}\right)}.$$

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#### CATAPHORESIS. PART III. A COMPARISON OF RESULTS OF MEASUREMENTS THE THE TRANSPORT AND MOVING BOUNDARY METHODS, AND A THEORY OF THE LATTER METHOD.

By D. C. Henry, M.A., and John Brittain, Ph.D.

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Apart from methods which utilise the microscopic observation of individual particles, all quantitative determinations of the cataphoretic mobility of colloidal micelles depend on one of two principles. In the "transport method" we measure the quantity of colloid which is carried across unit plane perpendicular to the direction of motion during the passage of a known quantity of electricity. In the "moving boundary method" we observe the rate of displacement, under a given potential gradient, of a visible boundary between colloidal solution and some supernatant liquid.

Although many investigations of each of these methods are on record, it is noteworthy that in almost all of them self-consistency of the results obtained by a single method has been tacitly accepted as a criterion of their correctness. This is certainly not a safe assumption, since, especially in the moving boundary method, there are difficulties of interpretation which, quite apart from experimental error, render the results subject to uncertainty, and which, in our opinion, have not as a rule been ade-

quately appreciated.

The present investigation is primarily a comparison of the results obtained by the transport and the moving boundary methods applied to the same sol as nearly as possible at the same time, necessarily preceded by an examination of each method separately. Incidentally a critical consideration of the two methods has led us to the belief that the transport method, suitably applied, leads to values which are correct within experimental error, but that the results of the moving boundary method, as usually interpreted, are incorrect. At the same time, we find that the Kohlrausch-Weber theory of ionic displacements provides a basis on which moving boundary results may also be correctly interpreted.

In the experiments recorded below, a silver sol prepared by a modification of the Kohlschütter method was employed as being conveniently applicable to both methods, since on the one hand it is highly coloured, and on the other is obtainable in fair concentration and is amenable to precise estimation by volumetric methods. Throughout the work the sol was prepared in batches of 2 litres, separate batches being distinguished by successive letters of the alphabet. To gm. of pure silver nitrate was dissolved in 200 c.c. of distilled water and the oxide precipitated with a slight excess of caustic soda. After washing free from alkali by repeated

<sup>&</sup>lt;sup>1</sup> Parts I and II of this series appeared in Proc. Roy. Soc., 143A, 106 and 130, 1931.

decantation with hot water, the precipitate was suspended in 2 litres of distilled water containing 1 gm. of sodium citrate. The mixture was maintained at  $60^{\circ}$  C. and washed hydrogen from a Kipp's apparatus passed through it for three hours. The resulting sol was filtered, dialysed in collodion thimbles for ten days with one change of water per day, again filtered and stored for use in Pyrex flasks. The final product was a dark coloured sol, clear by transmitted light, but strongly opalescent by reflected light, containing about 400 mg. of silver per litre and having a specific conductance of from 1 to  $7\times 10^{-5}$  reciprocal ohms cm.²/cm. Except for the formation, after a few days, of a slight sediment which completely redispersed on shaking, it was stable for months, although a continuous slow increase of conductivity occurred with ageing. Direct experiment showed that there was no measurable settling during the period of an experiment.

All determinations were carried out at 25° C. in an air thermostat controlled to  $\frac{1}{2}$ °. All vessels in which sol was contained were of Pyrex or Jena normal glass, and were rigorously cleaned by treatment with chromic acid followed by steaming or washing in distilled water. The first four series of experiments (A, B, C and D) were invalidated by insufficient attention to the latter part of the process, serious alterations in the conductivity of the sols being traced to this cause. In all subsequent experiments (except E3, which was used as a control), at least two hours' soaking in distilled water was used, and was found to be sufficient.

## 2. The Transport Method.

In principle this method resembles that of Hittorf for the determination of ionic transport numbers; it has been applied to colloidal systems by a number of workers. After a careful consideration of the methods employed by Duclaux, Varga, Wintgren, Engel and Pauli and Paine, that of Paine was chosen for our experiments. It possesses the advantage of simplicity, in that the introduction of the sol and its final removal in two sections is extremely easy. The bulk of the sol does not come into contact with taps, and the region in which the transport is effectively measured is located in the middle of the homogeneous sol column, far removed from any boundaries and from disturbances due to electrode processes.

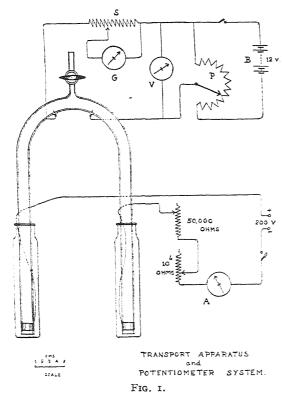
After some preliminary trials, the apparatus finally adopted was that shown in Fig. 1. The inverted U-tube had an internal diameter of 1.5 cm., a length of 65 cm. and a capacity of 105 c.c. Owing to the close fitting cylindrical form of the electrode vessels the volume of sol required for an experiment could be limited to 200 c.c., thus increasing the relative precision of the analytical determinations. The main electrodes, by which current was admitted to the system, consisted of strips of platinum foil I cm. wide tightly wrapped round the outside of the extremities of the U-tube. By this arrangement, as Paine points out, products of electrolysis, whether lighter or denser than the sol, are largely confined to the electrode vessels. Current was taken from the 200-volt mains through variable resistances; A was a micro-ammeter to register the total current flowing. Subsidiary electrodes, consisting of platinum points sealed through the bend of the U-tube at a distance of about 4 cm. apart, were used to control the potential gradient in the sol column, and were connected to a potentiometer system as shown; P was a dial pattern

<sup>&</sup>lt;sup>2</sup> J. Chim. physique, 7, 405, 1909.
<sup>3</sup> Kolloidchem. Beihefte, 11, 1, 1919
<sup>4</sup> Z. physik. Chem., 103, 258, 1922; 107, 403, 1923; 109, 378, 1924.

<sup>&</sup>lt;sup>5</sup> Ibid., **126,** 247, 1927. <sup>6</sup> Trans. Faraday Soc., **24,** 412, 1928.

potentiometer, GS a shunted galvanometer, and V a high resistance voltmeter by means of which the potential difference at balance could be read,

The U-tube was filled by suction and a current of a few tenths of a milliampère passed for a period of about two hours. The tap was then opened and the sol allowed to fall into the electrode vessels. The silver in each vessel, including any which had adhered to the electrodes, was brought into solution with a little nitric acid, and the liquids from each



vessel evaporated to about 25 c.c. silver content was determined by titration with N/100 ammonium thiocyanate with ferric alum as indicator, using a calibrated microburette. The titration was found to be reproducible to within 0.3 per cent., and since the ratio of silver transported to total silver was usually about 1/10, this ratio should be determinable to within about 3 per cent. This estimate is confirmed by the analyses made in series A to D, in which the silver content of the two electrode compartments after electrolysis, and the total silver content of the original sol, were separately determined for each several experiment. In the fifteen experiments of these series,

the sum of the first named quantities agreed with the last to within 0·25 per cent. on the average, with a maximum discrepancy of 0·5 per cent., while the anode gain and cathode loss of silver agreed with their mean value to within 2·5 per cent. on the average with a maximum discrepancy of 5·2 per cent. In view of the consistency of these analytical results, the mobility calculations in subsequent series were carried out by assuming the total silver equal to the sum of that found in the two electrode compartments, the former quantity being analytically determined (except in series E and N) once only for each batch of sol.

It can be shown (v. Paine,6) that

$$u = \frac{m}{M} \frac{\kappa}{it} = \frac{m}{M} \frac{D}{Vt}$$
 . . . (IA, IB)

where u is the mobility of the colloidal micelle,

m the mass of colloid transported from cathode to anode compartments,

M the mass of colloid per c.c. of the original sol,

κ the specific conductance of the sol at the point where separation into two parts is to take place, viz. at the top of the bend,

t the time of electrolysis in seconds,

it the quantity of electricity passed, in coulombs,

V the potential difference (presumed constant) between any two points in the liquid column not subject to disturbance by the products of electrolysis,

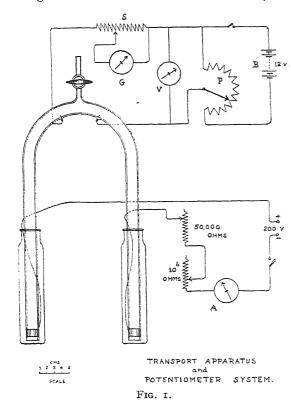
and D is a constant, depending on the form of the apparatus and the position of the points referred to, which is to be determined by calibration with an electrolyte of known specific conductance.

Paine employed equation (IB), measuring V between the main electrodes on the assumption that the potential gradient was uniform and constant throughout the whole length of the U-tube. The conductivity of his sols was very low and the current intensity correspondingly small, so that this assumption may have been justified. With our sols, of much higher conductivity, this was not so, for the accumulation of electrode products produced a notable diminution in the resistance of the apparatus as a whole during the course of an experiment. Our practice was to increase the external resistance from time to time so as to maintain V, as measured between the subsidiary electrodes, at a constant value, which was then employed in equation (IB). In the absence of polarisation at the subsidiary electrodes and of any contamination of the sol column lying between them, it is evident that this procedure should also result in a constant value of i, the substitution of which in equation (IA) should lead to the same value of the mobility. It was the failure to obtain even approximately a constant current which led to the discovery of the inadequacy of the cleaning technique in series A to D, and necessitated their rejection. In subsequent series the current was accurately constant during the greater part of each run, but showed a small increase in the initial, and occasionally in the final stages; except in series L, this increase did not amount to more than about I per cent. Correspondingly, the mobilities calculated by (IA) and (IB) were more nearly coincident. The cause of the residual discrepancy is uncertain, although it seems possible that that part of it which arises towards the end of the experiment may be due to a slight incursion of electrode products or to the dissolution of impurities from the glass. The initial rise of current may be connected with some slight polarisation of the subsidiary electrodes; it was naturally not possible to have the potentiometer accurately in balance at the very start. Some calibration experiments with 0.0002 N potassium chloride, in which i and V were varied over a wide range, are inconclusive on this point. The plot of i against V passed through the origin almost, if not quite, to within the accuracy of the measurements, but the "best straight line" through the points, determined by the method of medians, indicated the existence of a polarisation of about a tenth of a volt. This is of the order required to account for a I per cent. rise of current as the polarisation dies away after the more exact balance of the potentiometer system has been secured. In the hope of settling the question, reversible electrodes with agar bridges were substituted for the platinum subsidiary electrodes, in the manner indicated in Fig. 2, in series N and O, but no improvement resulted, and the i, V plot still indicated some polarisation. If polarisa-

<sup>&</sup>lt;sup>7</sup> It is possible that the behaviour under discussion is not due to polarisation at all, but to the known effect of relative motion of electrode and electrolyte (v. Charmandarjan and Perwuschin, Z. Electrochem., 36, 248, 1930; Procopui,

potentiometer, GS a shunted galvanometer, and V a high resistance voltmeter by means of which the potential difference at balance could be read,

The U-tube was filled by suction and a current of a few tenths of a milliampère passed for a period of about two hours. The tap was then opened and the sol allowed to fall into the electrode vessels. The silver in each vessel, including any which had adhered to the electrodes, was brought into solution with a little nitric acid, and the liquids from each



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V the potential difference (presumed constant) between any two points in the liquid column not subject to disturbance by the products of electrolysis,

and D is a constant, depending on the form of the apparatus and the position of the points referred to, which is to be determined by calibration with an electrolyte of known specific conductance.

Paine employed equation (1B), measuring V between the main electrodes on the assumption that the potential gradient was uniform and constant throughout the whole length of the U-tube. The conductivity of his sols was very low and the current intensity correspondingly small, so that this assumption may have been justified. With our sols, of much higher conductivity, this was not so, for the accumulation of electrode products produced a notable diminution in the resistance of the apparatus as a whole during the course of an experiment. Our practice was to increase the external resistance from time to time so as to maintain V, as measured between the subsidiary electrodes, at a constant value, which was then employed in equation (1B). In the absence of polarisation at the subsidiary electrodes and of any contamination of the sol column lying between them, it is evident that this procedure should also result in a constant value of i, the substitution of which in equation (IA) should lead to the same value of the mobility. It was the failure to obtain even approximately a constant current which led to the discovery of the inadequacy of the cleaning technique in series A to D, and necessitated their rejection. In subsequent series the current was accurately constant during the greater part of each run, but showed a small increase in the initial, and occasionally in the final stages; except in series L, this increase did not amount to more than about I per cent. Correspondingly, the mobilities calculated by (IA) and (IB) were more nearly coincident. The cause of the residual discrepancy is uncertain, although it seems possible that that part of it which arises towards the end of the experiment may be due to a slight incursion of electrode products or to the dissolution of impurities from the glass. The initial rise of current may be connected with some slight polarisation of the subsidiary electrodes; it was naturally not possible to have the potentiometer accurately in balance at the very start. Some calibration experiments with 0.0002 N potassium chloride, in which i and V were varied over a wide range, are inconclusive on this point. The plot of i against V passed through the origin almost, if not quite, to within the accuracy of the measurements, but the "best straight line" through the points, determined by the method of medians, indicated the existence of a polarisation of about a tenth of a volt. This is of the order required to account for a I per cent. rise of current as the polarisation dies away after the more exact balance of the potentiometer system has been secured. In the hope of settling the question, reversible electrodes with agar bridges were substituted for the platinum subsidiary electrodes, in the manner indicated in Fig. 2, in series N and O, but no improvement resulted, and the i, V plot still indicated some polarisation.7 If polarisa-

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tion actually occurs, the observed values of V may be slightly in error, and we have therefore adopted the values of the mobility given by equation (1A) as the more reliable, determining the specific conductance in accordance with well-accepted practice in a Wheatstone bridge, using audio-frequency current from a valve oscillator together with a correctly designed conductivity cell and the usual devices for balancing cell

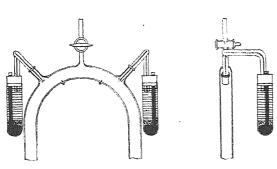


FIG. 2.

capacity. Even if it is admitted that the final rise of current intensity is due to contamination, this effect will be of short duration and is in any case small

Thermal disturbances are probably negligible, for with the largest currents we employed the

total rise of temperature in a two hours' run would be less than 0.3° C., and in view of the fact that the measurements are effectively made in

Series.	No.	mhos × 10 <sup>-5</sup> .	u (1A). cm./sec. × 10 <sup>-5</sup> .	# (IB). cm./sec. × 10 <sup>-5</sup> .	Series.	No.	mhos × 10 <sup>-5</sup> .	u(IA). cm./sec. × 10 <sup>-5</sup> .	u (1B). cm./sec. × 10 <sup>-5</sup> .
E	1 2 4 5	1.69 1.66 1.66 1.66 Mean	36·3 36·8 35·3 37·3 : 36·4 ± 0·6	36·5 36·8 34·8 36·7 36·2 ± 0·7	К	2 4 6	3·10 3·10 Mean	36·9 38·1 38·1 : 37·7 ±0·5	38·1 37·9 38·0 38·0±0·1
F	I 2	3·00 3·03	37·3 37·6	37·6 37·2	L	2 4	6·95 6·99 Mean	36·5 37·1 : 36·8 ±0·3	39·I 41·8 40·5 ± I·4
	3 4 5	2·99 2·99 2·97 Mean	36·5 36·5 36·3 : 36·8 ± 0·5	36·6 36·8 36·4 36·9 ± 0·4	М	2 4 5	0.974 1.004 1.04 Mean	32·3 31·7 32·3 : 32·1 ± 0·3	34·9 33·8 33·8 34·2 ±0·5
G	1 2 3 4	1·23 1·23 1·24 1·24	32·0 33·0 34·3 32·7	33·I 33·9 34·3 32·8	N	2 4	1·57 1·58	35·3 34·1 : 34·7 ±0·6	34.0 33.8 33.9 ±0.1
		Mean	: 33·0 ± 0·7	33·5 ± 0·6	0	2 4	1·73 1·73 Mean	37·2 33·8 : ?	37·3 33·5

TABLE I.—RESULTS OF THE TRANSPORT METHOD.

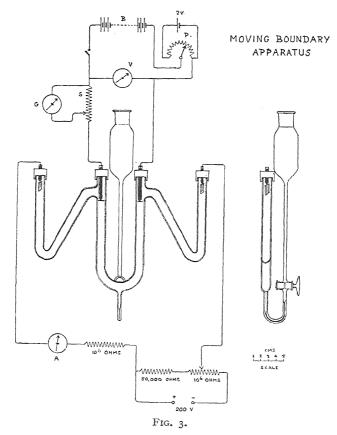
J. Chim. physique, 27, 29, 1930). This explanation would account for the fact noted by Mukherjee (J. Indian Chem. Soc., 4, 493, 1927), and also observed by us, that the effective (electrical) distance between the subsidiary electrodes appears to depend on the conductivity of the liquid used to measure it. In our calibrations potassium chloride of approximately the same conductivity as the sol was always employed.

a homogeneous part of the sol, it is probable that the influence of convection currents would in any case be relatively small. For the same reason mechanical diffusion will be inoperative. There would appear to be no other factors which could invalidate the results, and we are of the opinion that the figures obtained by the use of equation (IA) probably represent true values of the mobility of the colloidal micelle with an uncertainty of from 3 to 4 per cent., the greater part of which is due to analytical difficulties.

Table I. includes every experiment performed by the transport method in the course of the research, with the exception of certain preliminary experiments carried out before the analytical method had been worked out, and of series A to D (and experiment E3) which were rejected for the reason already given. Mobilities calculated from both equations are included; u (IA) is the value adopted as most probably correct.

## 3. The Moving Boundary Method.

After some preliminary trials, an apparatus was adopted of the pattern recommended by Kruyt (Fig. 3). The boundaries between sol and super-



natant liquid are formed in the central U-tube, of r cm. internal diameter, by slow filling from below. It may be noted that the use of taps to form

the boundaries, as employed in some older types of apparatus, is quite unnecessary and in many ways undesirable; perfectly sharp boundaries can be formed without their use in times of the order of half an hour by careful attention to the conditions of inflow of the liquid. The sol must be run in very slowly until the boundary has divided into two on the bottom bend of the U-tube, after which it may be run in much faster.

The main, or current-bearing electrodes of platinised platinum foil are situated in the side tubes, which serve to protect the main U-tube from the products of electrolysis. The potential fall in the U-tube was determined by means of wheel-shaped subsidiary electrodes of platinised platinum inserted at the top of each limb. The electrical arrangements were identical with those employed in the transport method, except that the potentiometer system was given a wider range by means of the supplementary battery B.

The fundamental difficulty of the moving boundary method is the determination of the potential gradient under which the boundary is moving. Since the colloidal micelles themselves contribute to the conductivity, it is easily seen that, whatever supernatant liquid is used, it is not possible to maintain a completely uniform potential gradient along the U-tube. Mukherjee 8 attempts to overcome this difficulty by measuring the potential difference across the boundary by means of reversible electrodes inserted in small side tubes sealed to the U-tube, and assumes that this represents the gradient under which the boundary moves, while Kruyt 9 introduces a method of calculation which assumes that a boundary located above its initial position moves in a medium of conductivity equal to that of the supernatant liquid, while a boundary which is below its initial position moves in a medium of conductivity equal to that of the sol. The theoretical treatment to be given in § 4 will show that neither Mukherjee's nor Kruyt's assumptions are completely valid. On the other hand, Kruyt's procedure leads to values which are easily related to the theoretical formulæ, and in consequence our results will in the first instance be presented in terms of his calculations.

It can readily be shown (v. Kruyt 9) that

$$u_{KA} = v_A h_2 / e_2 = v_A \kappa_2 / i$$
  
 $u_{KB} = v_B h_1 / e_1 = v_B \kappa_1 / i$ ,

and

where  $u_{KA}$ ,  $u_{KB}$  respectively denote the mobilities of the colloidal micelle as calculated on Kruyt's assumptions from the motion of the boundaries which are above and below their initial positions,

v<sub>A</sub>, v<sub>B</sub> denote the actual observed velocities of the respective boundaries,

 $h_1$  is the effective length of the sol column,

 $h_2$  the sum of the lengths of the supernatant liquid columns,

 $e_1$  is the potential drop in the sol column,

 $e_2$  the sum of the potential drops in the supernatant liquid columns,  $\kappa_1$ ,  $\kappa_2$  are the specific conductances of the sol and supernatant liquid, and i is the current density in amperes per square centimetre. Further, if Kruyt's assumptions are correct, we should have

$$v_{\rm A}/v_{\rm B} = \kappa_{\rm 1}/\kappa_{\rm 2}$$
 and  $u_{\rm K} = u_{\rm KA} = u_{\rm KB} = (v_{\rm A}h_2 + v_{\rm B}h_{\rm 1})/E$ , (2)

<sup>&</sup>lt;sup>8</sup> Proc. Roy. Soc., 103A, 102, 1923. 
<sup>9</sup> Kolloid Z., 44, 22, 1928.

where  $u_{\mathbb{K}}$  should represent the true mobility of the colloidal micelle and E is the total potential drop between the subsidiary electrodes.

In most of the experiments to be reported, the supernatant liquid consisted of ultrafiltrate from the sol itself, separated by means of a porous porcelain vessel impregnated with acetic collodion ("Celloidin" 4 gm., potassium carbonate I gm., glacial acetic acid 100 c.c.) and washed thoroughly in water. In a few experiments, as will be indicated in the tables, other supernatant liquids were used. During the experiment, the external resistance was adjusted to maintain a constant value of E; in no experiment was the current increase more than I per cent. The positions of the boundaries were read with a small cathetometer, and in the case of sharp boundaries could be fixed within 0.2 mm. The gross displacement usually observed was from I to 2 cm. The potential gradient employed was between 2 and 2.5 volts per cm., and the duration of an experiment from 30 to 40 minutes.  $h_1 + h_2$ , the effective distance between the subsidiary electrodes, which on account of the curvature of the tube was not identical with the geometrical distance, was obtained in terms of centimetres of the straight limbs by a calibration with 0.0004 N potassium chloride solution; the resistance included between the subsidiary electrodes was determined with the latter in various known positions in the straight limbs. The final value adopted for  $h_1 + h_2$ , deduced from ten separate calibration readings, was 26.9 cm., with a probable uncertainty of less than I per cent.

Table II summarises all the experiments made by the moving boundary method in the course of the work. The nature of the supernatant liquid is indicated in column three.

While the results presented in Table II. admittedly leave something

to be desired, certain general regularities are clearly discernible.

In the first place, the results of reverse experiments are less concordant than those of direct experiments; this is only to be expected, since the boundaries in the former were usually somewhat hazy. If reverse experiments are excluded from consideration, the degree of concordance of comparable experiments with a given sol, as judged by the values of  $u_{KA}$  and  $u_{KB}$ , ranges between 1 and 5 per cent., and averages about 2 per cent. In favourable cases, then, experiments by this method have a slightly higher precision than those by the transport method.

Secondly, Kruyt's assumptions are not confirmed, since  $u_{\rm KA}$  and  $u_{\rm KB}$  are certainly not equal within experimental error, nor is the ratio  $v_{\rm A}/v_{\rm B}$  equal to  $\kappa_1/\kappa_2$ . Consequently we cannot assume the mobilities calculated by Kruyt's method to be correct values. If we are right in assuming the results of the transport method to be substantially correct, Table III, in which are collected the mean results of the various groups of experiments, shows that in a large majority of cases  $u_{\rm KA} > u_{\rm KB} > u$ . While the exceptions must not be lost sight of, we shall find that the more usual behaviour has a significance in the theory to be developed below.

## CATAPHORESIS

TABLE II.\*—RESULTS OF MOVING BOUNDARY EXPERIMENTS.

Series.	No.	SL.	κ <sub>1</sub> .	κ <sub>2</sub> ,	u <sub>KA</sub> .	u <sub>KB</sub> .	u <sub>K</sub> .	$\frac{v_{\rm A}}{}$ .	κ <sub>1</sub>
Series.	No.	, SL,	mhos >	< 10 <sup>-5</sup> .	cm.	/sec. × 10	o-δ,	$\overline{v_{\mathrm{B}}}$	$\frac{\kappa_1}{\kappa_2}$ .
H (a)	I R 2 R 3 R	UF	3.19	3.61	26·0 28·7 25·2 24·7 24·0 26·0	25.5 26.2 26.9 29.8 28.7 32.8	25·7 27·8 26·0 26·8 27·2 28·9	1·17 1·03 1·06 0·94 0·92 0·87	I·13 I·13
I (a)	1 R 2 R 3 R 4 R	,, ,, ,, ,, ,,	1.91 ———————————————————————————————————	2·12 2·12 ——————————————————————————————	34·I 34·4 38·4 35·7 39·I 37·9 38·2 36·6	35·2 34·4 32·5 36·0 34·4 34·9 30·8 34·8	34·7 34·4 34·6 35·9 36·1 36·0 33·7 35·5	1.07 1.11 1.31 1.10 1.26 1.21 1.38 1.16	I·II
(b)	5 R 6 R	UFC	2·55 2·55 2·55 2·55	2·90 2·90 2·99 2·99	43°4 42°4 44°0 42°0	35·3 37·0 36·5 38·2	38·5 39·0 38·9 39·8	1·40 1·30 1·37 1·29	I·I4 I·I4 I·I7 I·I7
J	R R R R	UFC	1.92 1.92 2.25 2.25 2.52 2.52	2·02 2·02 2·43 2·43 2·56 2·56	36·5 36·6 34·2 35·3 36·0 38·6	31·5 32·5 32·3 31·3 33·6 33·2	33·2 33·9 33·0 32·8 34·4 35·2	1·22 1·19 1·15 1·23 1·09 1·18	1.05 1.05 1.08 1.08 1.02
K	1 5 8	UF "	2·93 2·93 2·93	3·10 3·16 3·10	41·2 42·2 42·1	39·4 38·7 38·9	40·1 39·9 40·1	1·15 1·15	1.09 1.09
	3 R	SC ,,	3·02 3·02	3.10 3.10	31·2 41·1	46·9 35·4	41·1 37·5	0.70	1.06 1.06
	7	С	3.11	3.10	47.0	42.1	44.6	1.12	1.00
L	3	UF "	6·70 6·81	6·99 6·81 ?	39·2 39·9	37·4 37·4	38·0 38·6	1.00	1.04
	5	UFC	7.14	6.95	39.6	38.1	38.6	1.01	0.97
	6	С	6.99	6.99	45.3	39.5	41.4	1.12	1.00
M	3	UF "	0.932 0.942	1.004	34·5 33·3	39·5	36·8	0.97 0.96	1.08
N	3	UF "	1·43 1·45	1.56	39·0	37·6 37·8	38·3	1.11	1.08
(c)	5	UF	1.45	1.46	39.7	42.6	41.5	0.94	1.00
0	3 R 5 6 7 8	UF ,, ,, ,, ,,	1.60 1.59 1.59 1.57 1.57 1.58 1.61	1.73 1.73 1.73 1.73 1.73 1.73 1.73	40·2 40·9 41·7 41·8 40·7 40·8 40·8	38·8 39·6 40·0 38·4 37·7 38·8 37·7	39·3 40·1 42·3 39·7 38·8 39·6 38·8	1·12 1·12 1·11 1·20 1·19 1·15 1·17	1.08 1.09 1.10 1.10 1.10

[See footnote on page 807.

	TABLE III.—COLLECTED	MEAN R	ESULTS BY	THE MOVING	BOUNDARY METH	on.
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Sol.	SL.	u <sub>KA</sub> .	<b>+</b> .	u <sub>KB</sub> .	<b>*</b> -	u(calc.).	u <sub>TR</sub> .
301,	31,			cm./sec.	× 10 <sup>-5</sup> .		
Н	UF	25.1	0.7	27.0	1.1	_	
I	UF UFC	37·4 45·7	0.3 0.4	33·2 35·9	1·6	33-8	} -
J	UFC	35.6	0.0	32.5	o·8	34.0	
K	UF SC C	41·8 31·2 47·0	o∙6 — —	39·0 46·9 42·1	o·3 —	38·5 —	37.7
L	UF UFC C	39·5 39·6 45·3	o·3 —	37·4 38·1 39·5	0·0 —	38·3 —	36.8
$\mathbf{M}$	UF	33.9	o·6	38.5	0.7		32.1
N	UF	39.0	0.0	37.7	0.1	34.8	34.7
0	UF	40.9	0.3	38.5	0.6	<b>36·</b> 6	{ 37·2 33·8

## 4. A Theory of Moving Boundary Cataphoresis.

So long as the intermicellar liquid in a colloidal solution remains of sensibly constant composition, the micelle itself may be considered as an ion of fixed charge. If, further, the ionic concentrations (including that of the micelle) are small, the ionic mobilities can be presumed constant, and the motion in an electric field should be governed by the Kohlrausch-Weber theory of ionic displacements in dilute solution. We find that this theory provides an explanation of the failure of Kruyt's assumptions, and indicates methods by which the correct value for the mobility of a colloidal micelle may be deduced from moving boundary experiments. It will be convenient for the present purpose to develop the Kohlrausch-Weber theory in a form slightly different from that of

<sup>10</sup> F. Kohlrausch, Wied. Ann., 62, 209, 1897; H. Weber, Sitz. Preuss. Ahad. Wiss., 1897, p. 936.

<sup>\*</sup>The letter R in column two indicates the reverse movement of the boundaries mployed in the preceding line; the reverse experiment was carried out immediately after the direct. In column three supernatant liquids (SL) are indicated as follows: UF ultrafiltrate, C sodium citrate, UFC ultrafiltrate plus sodium citrate, SC silver oxide (saturated solution) plus sodium citrate.

<sup>(</sup>a) In the early stages of the research, it was not realised that the conductivity was liable to an appreciable alteration during the period (about one week) required to complete a series; conductivity determinations were therefore carried out once only for each batch of sol in conjunction with the first experiment made with it. The specific conductances for the subsequent experiments of groups H and I (I to 4) are therefore, as indicated in the table, not known with certainty; for the calculation of  $u_{KA}$  and  $u_{KB}$  the value as determined at the beginning of the series has been assumed.

<sup>(</sup>b) Three weeks elapsed between experiments I4 and I5.

<sup>(</sup>c) The sol for this experiment was diluted to four times its volume with ultrafiltrate.

the original, and although we shall only be able to obtain a solution for the case in which not more than three sorts of ions are present, the differential equations for the more general case will first be established.

Consider a liquid containing in dilute solution any number of ionic species A, B, . . . S, . . ., and subjected to an electric field uniformly directed parallel to the x-axis of co-ordinates. Let the mobility of the S ion be  $u_s$  cm./sec. per volt/cm. At time t and co-ordinate x let the potential gradient be X volts/cm., the specific conductance  $\kappa$  reciprocal ohms cm.²/cm., and the concentration of the S ion S gm.-equivalents per c.c. It will simplify the equations to use directed mobilities, and concentrations expressed in units of electric charge carried; we therefore write: for a cation  $s = u_s$ ,  $\sigma = SF$ , and for an anion  $s = -u_s$ ,  $\sigma = -SF$ , where F is the Faraday constant (96500 coulombs). Let i be the current density, which need not be constant in time, but must be independent of x.

By considering the rate of entry and departure of S ions in an element of volume of I cm.<sup>2</sup> cross-sectional area perpendicular to the direction of the electric field, we find that, for each ion

$$\frac{\partial \sigma}{\partial t} = s \frac{\partial (X\sigma)}{\partial x} = is \frac{\partial (\sigma/\kappa)}{\partial x}$$

$$\kappa = \Sigma s \sigma$$

$$\Sigma = s \sigma$$
(3)

Further

while for electric neutrality  $\Sigma \sigma = 0$ 

These equations define the motion in all regions where there is no discontinuity in the concentration of any ion.

Suppose now that there exists a discontinuity in the concentration of the S ion at the point  $x=x_0$ , the respective values of  $\sigma$  and  $\kappa$  immediately to the left and right of the discontinuity being  $\sigma'$ ,  $\kappa'$  and  $\sigma''$ ,  $\kappa''$ . Consider a fixed element of volume, of I cm.² cross-sectional area, enclosing the instantaneous position of the discontinuity. In time  $\delta t$  (small enough for the discontinuity to remain within the volume element throughout) the nett gain of S ions in the volume element is  $is(\sigma''/\kappa'' - \sigma'/\kappa')$ .  $\delta t$ . This will produce a shift of the discontinuity through a distance  $\delta x_0$  such that  $(\sigma'' - \sigma')$ .  $\delta x_0$  also represents the nett gain of S ions. It follows that the motion of the discontinuity is given by:

$$\frac{dx_0}{dt} = is \frac{\sigma''/\kappa'' - \sigma'/\kappa'}{\sigma'' - \sigma'}. \qquad (4)$$

Equations (3) and (4) are only readily soluble when the ion species are restricted to three in number, which we will denote A, B, and C; their directed mobilities and electro-concentrations (as defined on p. 804 will be denoted by a, b, c and  $\alpha$ ,  $\beta$ ,  $\gamma$ . Eliminating <sup>11</sup>  $\beta$  and  $\gamma$  from equations (3) we obtain:

$$\frac{\partial \alpha}{\partial t} = ia \frac{\partial (\alpha/\kappa)}{\partial x}$$

$$\frac{\partial \kappa}{\partial t} = i(\alpha - b)(\alpha - c) \frac{\partial (\alpha/\kappa)}{\partial x}$$
(5)

and

 $^{11}$  Most conveniently with the help of the substitutions  $\theta_a=a\alpha/\kappa,$  etc., with  $\theta_a+\theta_b+\theta_c=\text{I}.$ 

whence it follows that:

$$\frac{\partial \kappa}{\partial t} = \frac{(a-b)(a-c)}{a} \frac{\partial \alpha}{\partial t},$$

and

$$\kappa - \frac{(a-b)(a-c)}{a}\alpha = f_a(x),$$

where  $f_a(x)$  is independent of t.

Setting

$$\phi_a = I - \frac{(a-b)(a-c)}{a\kappa}\alpha,$$

so that

$$\kappa \phi_a = f_a(x),$$

equation (5) leads to

$$\left(\frac{\partial x}{\partial t}\right)_{\phi} = -ia\phi_a^2/f_a(x) \quad . \tag{6}$$

which gives the velocity of a point of constant  $\phi_a$  in the absence of a discontinuity. By equation (4) the motion of a discontinuity in A is given by:

 $\frac{dx_0}{dt} = ia \frac{\phi_a^{"} - \phi_a^{"}}{\kappa'' - \kappa' - f_a^{"} + f_a^{"}}$ 

where  $f_a$  and  $f_a$  are the respective values of  $f_a(x)$  in the continuous regions immediately adjacent to the discontinuity. Where the latter is moving through a region which was initially continuous,  $f_a$  =  $f_a$  and:

$$\frac{dx_0}{dt} = iaf_a \frac{(1/\kappa'' - 1/\kappa')}{\kappa'' - \kappa'} = -ia\frac{f_a}{\kappa'\kappa''} \quad . \tag{7}$$

It is easy to show by direct substitution, having regard to the condition  $\alpha + \beta + \gamma = 0$ , that <sup>12</sup>:

$$a\phi_a = b\phi_b = c\phi_c = -(abc/\kappa)(\alpha/a + \beta/b + \gamma/c).$$

It follows from equations (6) and (7) that the velocity, whether of a point of constant  $\phi$  or of a discontinuity, is the same for all ions, the respective values of  $\phi$  for the different ions being connected by the above relation.

Let us now suppose that at t=0 the only discontinuity is at x=0, the ionic concentrations to left and right of this point having initially two sets of constant values which we will distinguish by the subscripts I and 2. The subsequent velocity of each continuous region will be uniform and constant, and will respectively be given by  $^{13}$ 

$$v_1 = -ia\phi_1^2/f$$
,  $v_2 = -ia\phi_2^2/f$ , . . . (8)

where the numerical subscript to be assigned to f depends on whether the motion is to the right or to the left. If ia is positive, it is the latter and we must write  $f_1$ , if negative, the former and we write  $f_2$ . We will assume the direction of the current so arranged that the motion is to the right.

If  $\phi_1 > \phi_2$ , the left-hand section overtakes the right (see Fig. 4A), and in the region of overlap,  $\phi$  would appear to be two-valued. This

<sup>&</sup>lt;sup>12</sup> It will be observed that  $-af_a(x)/abc$  is the "beharrliche funktion" of Kohlrausch.

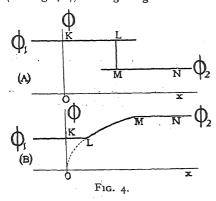
 $<sup>^{13}</sup>$  In what follows, the symbols  $\theta,\,\phi$  and f will always refer to the A ion, and the literal subscript can be omitted.

is impossible, and there must be a discontinuity LM somewhere within this region, whose velocity will be given by

$$v_0 = -iaf_2/\kappa'\kappa''$$

where  $\kappa'$ ,  $\kappa''$  refer to regions immediately left and right of LM. But for the region KL,  $\kappa'\phi_1 = f_2$  and for the region MN  $\kappa'' = \kappa_2$ , so that we have  $v_0 = -ia\phi_1/\kappa_2$ .

If, on the other hand,  $\phi_1 < \phi_2$ , the left-hand region lags behind the right (see Fig. 4B), leaving a region in which  $\phi$  is left undetermined by equations



as mathematical requirements are concerned for a boundary which is initially quite sharp, this region may be filled either with a continuous range of values of  $\phi$  or with one or more discontinuities. The following treatment, for which we are indebted to Mr. A. F. Core, indicates that the former alternative (which Weber himself preferred) is the correct one in the case of a boundary which is initially sharp only in a "practical" sense:

(8). As Weber points out, so far

The integral of equation (6) is

$$\int f(x) \cdot dx + a\phi^2 \int idt + g(\phi) = 0, \quad . \quad . \quad (9)$$

where  $g(\phi)$  is a function of  $\phi$  only, whose form is to be determined by the initial conditions. These are adequately represented by allowing n to become very large in the expressions:

$$\begin{array}{c} f(x) = \frac{1}{2}(f_2 - f_1) \tanh nx + \frac{1}{2}(f_2 + f_1) \\ \phi(x, t)_{t=0} = \frac{1}{2}(\phi_2 - \phi_1) \tanh nx + \frac{1}{2}(\phi_2 + \phi_1). \end{array}$$

Substituting these expressions, and t=0, in equation (9), we obtain:

$$\frac{1}{2n}(f_2 - f_1) \log \cosh nx + \frac{1}{2}(f_2 + f_1) \cdot x + I 
= g\{\frac{1}{2}(\phi_2 - \phi_1) \tanh nx + \frac{1}{2}(\phi_2 + \phi_1)\},$$

where I is an integration constant. This is satisfied by:

$$g(\phi) = \frac{1}{2n} \{ f_2 \log (\phi_2 - \phi) - f_1 \log (\phi - \phi_1) - (f_2 - f_1) \log \frac{1}{2} (\phi_2 + \phi_1) \} - I.$$

On substituting this expression in equation (9) and letting  $n \to \infty$ , we find that, for  $\phi_1 < \phi < \phi_2$ ,

$$f_1 \cdot x + a\phi^2 \cdot \int idt = 0$$
 for  $x < 0$   
 $f_2 \cdot x + a\phi^2 \cdot \int idt = 0$  for  $x > 0$ . (10)

and

This corresponds to the continuous variation of  $\phi$  with x represented by the parabolic curve LM in Fig. 4B, and produces the effect of a diffuse boundary.

In a cataphoretic experiment with a U-tube, therefore, there will always be one sharp and one diffuse boundary. The experimentally

determined velocity of the latter will of course lie between  $v_1$  and  $v_2$  (equation 8), but its exact value, as given by equation (10), will depend on the value of  $\phi$  corresponding to the point in the diffuse band at which the observer judges the "boundary" to be located.

The corresponding relations for a boundary moving to the left are to be obtained by interchange of the suffixes I and 2. We can summarise the possible alternatives, with the prescribed initial conditions, in the following table, in which arithmetical values of the ionic mobilities have been introduced, and the equations written without directional sign;  $\phi_0$  denotes the value of  $\phi$  selected to define the position of the diffuse boundary. The conclusions hold for both anionic and cationic colloids.

$$\text{Case A: } \phi_1 < \phi_2 \begin{cases} \text{Boundary diffuse} \\ v_{\text{A}} = i u_a \phi_0^2 / \kappa_2 \phi_2 \\ v_{\text{KA}} = u_a \cdot \phi_0^2 / \phi_2 \end{cases} \quad \begin{array}{ll} \text{Boundary sharp} \\ v_{\text{B}} = i u_a \phi_0 / \kappa_1 \\ w_{\text{KB}} = u_a \cdot \phi_2 \end{cases}$$
 
$$\text{Case B: } \phi_1 > \phi_2 \begin{cases} \text{Boundary sharp} \\ v_{\text{A}} = i u_a \cdot \phi_1 / \kappa_2 \\ u_{\text{KA}} = u_a \cdot \phi_1 \end{cases} \quad \begin{array}{ll} \text{Boundary diffuse} \\ v_{\text{B}} = i u_a \phi_0^2 / \kappa_1 \phi_1 \\ w_{\text{KB}} = u_a \cdot \phi_0^2 / \phi_1 . \end{cases}$$

The behaviour of a boundary on reversal of the current depends on whether it is a sharp or a diffuse boundary at the moment of reversal. The processes which take place in the direct displacement will be exactly reversed "provided the conditions obtaining at the moment of reversal determine the subsequent behaviour uniquely in both directions" (Weber). Thus a diffuse boundary, on reversal, should retrace its path with the same velocity, becoming continually sharper, until, on passing through its original starting-point, it assumes the behaviour characteristic of a sharp boundary. On the other hand, a sharp boundary, on reversal, does not retrace its path in the same manner, but becomes diffuse and moves with the velocity characteristic of the latter type of boundary. The phenomena of reversal need not be enlarged on further since diffusion and other disturbing factors tend to prevent their realisation in practice, but it should be noted that the behaviour just described is in general agreement with our experimental observations.

It should be noted that the original discontinuity at x=0 does not, in general, disappear, but persists permanently at the same spot. Although  $\phi$  is continuous at x=0 after the boundary has moved away, the ionic concentrations and the conductance change discontinuously on passing from one side to the other of the zero point, a fact which would appear to invalidate Mukherjee's method of arriving at the potential gradient operative at the boundary. It follows that an advancing column of sol is not identical in composition with the original sol, but has a concentration determined by the condition that  $\alpha/\alpha + \beta/b + \gamma/c$  must have the same value on both sides of the moving boundary (cf. equation 8). Only if this condition was satisfied in the initial state does the sol column move up unchanged.

We will now turn to the special initial conditions which obtain in a typical moving boundary cataphoretic experiment. If A represents the colloidal ion, B an ion of the same sign and C an ion of the opposite sign, these conditions are:

for 
$$x < 0$$
 (sol),  $\alpha = \alpha_1$ ,  $\beta = \beta_1$ ,  $\gamma = -(\alpha_1 + \beta_1)$ , and for  $x > 0$  (SL),  $\alpha = 0$ ,  $\beta = \beta_2$ ,  $\gamma = -\beta_2$ .

Whether the colloidal micelle is anionic or cationic, we find that:

$$\begin{array}{l} \kappa_{1}/F = (u_{a} + u_{c})A_{1} + (u_{b} + u_{c})B_{1}, \\ \kappa_{2}/F = (u_{b} + u_{c})B_{2}, \\ \phi_{1} = (F/\kappa_{1}u_{a})\{u_{b}(u_{a} + u_{c})A_{1} + u_{a}(u_{b} + u_{c})B_{1}\}, \\ \phi_{2} = \mathrm{I}. \end{array}$$

If  $u_a>u_b$ ,  $\phi_1<\phi_2$  and  $u_{\rm KA}:u_{\rm KB}:u_a=\phi_0^2:$  I: I while if  $u_a< u_b$ ,  $\phi_1>\phi_2$  and  $u_{\rm KA}:u_{\rm KB}:u_a=\phi_1:\phi_0^2/\phi_1:$  I, where in each case  $\phi_0$  is intermediate in value between  $\phi_1$  and unity. The latter alternative, which requires that  $u_{\rm KA}>u_{\rm KB}>u_a$ , is clearly the one which corresponds to the majority of our experiments, as might indeed be expected since the only anion whose presence would appear likely in our silver sols is either citrate or hydroxyl, with mobilities respectively equal to 63 and 180  $\times$  10<sup>-5</sup> as compared with approximately 35  $\times$  10<sup>-5</sup> for the silver micelle. For the experiments in question we can therefore assume:

$$u_a = u_{\rm KA} \cdot \frac{1}{\phi_1} = u_{\rm KB} \cdot \frac{\phi_1}{\phi_0^{2^*}}$$
 . (11a, 11b)

Without experimental data of higher accuracy than we have so far been able to attain, it is not reasonable to expect any convincing quantitative confirmation of these equations, but with the help of the experiments of series K to O, which were carried out by both moving and transport methods, we have made some attempt to verify equation (IIa).

If we can assume the ultrafiltrate to be sensibly identical with the intermicellar fluid (not including the "outer sheet" of the electrical double layer of the micelles), its conductivity will be given by

$$\kappa_0/F = (u_b + u_c)B_1$$

and we shall have

$$\phi_1 = \frac{\kappa_0}{\kappa_1} + \frac{\kappa_1 - \kappa_0}{\kappa_1} \frac{u_b}{u_a}.$$

The second term in this expression is fairly small, and an approximate knowledge of  $u_a$  and  $u_b$  should suffice to determine  $\phi_1$ ;  $u_a$  can then be calculated from the observed value of  $u_{\rm KA}$ . The figures in the column headed u (calc.) in Table III were obtained in this way, assuming the ion B to be citrate; they are in fair agreement with the transport results  $u_{\rm TR}$ , showing an average discrepancy of about 5 per cent. Better agreement is obtained by assuming  $u_b$  to have a value between 90 and  $100 \times 10^{-5}$ , and possibly the presence of both citrate and hydroxyl ions may be suggested to account for this.

It is not possible, with the data at present available, to make any attempt to verify equation (IIb). It is, in fact, at first sight, surprising to find the agreement between comparable values of  $u_{\rm KB}$  as good as it is. The explanation is probably to be sought in the very high degree of opacity shown by the silver sols. We find, for example, that a typical sol still appears opaque under the conditions of our cataphoretic experiments when diluted four times. It follows that only a fraction—approximately one-quarter—of the depth of a diffuse band is visible as such to the eye, and since the setting will naturally be made quite close to the opaque margin, it is likely that  $\phi_0$  will have a fairly constant value for a given sol. But to determine what value would require some sort of photometric technique to be added to the cataphoretic experiment. The full depth of the diffuse band predicted by the theory is

from I to 2 mm. at the end of one of our runs, but since only a small fraction of this is appreciably translucent, the haziness is not very pronounced. In this connection it is interesting to refer to the notes made at the time  $^{14}$  by the observer responsible for the experiments presented in this paper. In series H (in which it is not on the average true that  $u_{\rm KA}>u_{\rm KB}$ ) both boundaries became sharper during the direct experiment, especially the falling one. In series L, M, N and O it is noted that the rising boundary was the sharper, in agreement with the theory. No comment was made on the sharpness of the boundaries in series I, J and K, so that presumably there was very little distinguishable difference between them. Another observer, working with the same apparatus and sols, states that almost without exception his rising boundary is the sharper.

A few further consequences of the theory are worthy of note:

Although the formulæ of the preceding pages, and in particular equations (II), should correctly represent the relationship between the experimentally determinable quantity  $u_{\rm KA}$  and the true mobility  $u_a$ , it must not be assumed that the latter necessarily represents the mobility of the micelle as it exists in the undisturbed sol. As has already been pointed out, the composition of the advancing sol column is in general different from that of the original sol, and is determined by the relations  $\phi = \phi_1$ ,  $f = f_2$ , where unaccented letters refer to magnitudes in the advancing column. On substitution and simplification, the first relation leads to the conclusion that  $A/B = A_1/B_1$ , while the latter gives

$$\frac{u_a + u_c}{u_a} A + \frac{u_b + u_c}{u_b} B = \frac{u_b + u_c}{u_b} B_2. \qquad . \tag{12}$$

The advancing column will therefore hold its constituent ions in the same relative proportion as in the original sol, but will in general undergo dilution or concentration. Only if equation (12) holds for the original sol and supernatant liquid will the sol column move up unchanged. But the mere dilution or concentration of a sol may alter the charge on the ionic micelle by disturbing the adsorption equilibrium of the ions which give it its charge, and is in fact a violation of the proviso laid down in the first sentence of § 4. The change in concentration is not by any means negligible; in some of our experiments with ultrafiltrate it would amount to some 10 or 20 per cent. It is highly probable that within certain limits the variation in cataphoretic velocity which is observed to result from alteration in the supernatant liquid arises from the effect under discussion.

The magnitude, and even the sign, of the change in true mobility which results from dilution cannot be predicted, for the adsorption equilibrium, and its connection with the mobility, are by no means simple. In the first place, it is probable that both ions, B and C, take part in the equilibrium, the resulting micellar charge being due to a preponderance in the adsorption of one or the other. Secondly, it is not the charge itself, but the potential difference of the electrical double layer, which is directly connected with the cataphoretic mobility, and this potential difference depends on the ionic distribution in both sheets of the double layer. So long as the electrical state of the micelle remains unaltered, we are entitled to regard it as an ion of fixed charge.

<sup>&</sup>lt;sup>14</sup> It should be emphasised that all our experiments were completed before any theoretical ideas were entertained.
<sup>15</sup> V. "Cataphoresis, Part I.," loc. cit.

The consequences of any alteration in its electrical state, however, involve the more complicated considerations indicated.

At the retreating boundary, analogous conditions hold, except that in this case it is the advancing column of supernatant liquid which changes in concentration, and the error under discussion does not arise. If the difficulty of locating the falling boundary could be overcome, as for instance, by utilising as ion B one with a smaller mobility than the micelle, or by locating the dense end of the diffuse band photometrically, the use of the falling boundary would undoubtedly be preferable to that of the rising.

One way of eliminating the difficulty entirely is to use a supernatant liquid of concentration determined by equation (13). In this case  $v_{\rm A}=iu_a/\kappa_1$ , and the correct value of  $u_a$  is immediately deducible from the motion of the rising boundary without any complications arising from a change of composition of the advancing column. This method has recently been advocated by Hacker, <sup>16</sup> who first makes an approximate estimate of the concentration of BC needed in the supernatant liquid by the use of an equation, in terms of specific conductances, which follows immediately from (13), and then carries out a series of trials with different concentrations until the conductivity of the rising column, as measured by the potential fall across two "Mukherjee side tubes," is found to be identical with that of the original sol. Except for the somewhat laborious necessity of selecting the correct supernatant liquid by trial, this method probably affords the most satisfactory application of the moving boundary technique.

When for any reason it is not convenient to apply Hacker's method, and especially if the change in concentration of the advancing column is not considered to be important, equation (12) provides an excellent method of evaluating  $\phi_1$ , which can be used to deduce  $u_a$  from the motion of the rising boundary. For we have  $\phi_1 \kappa = \phi \kappa = f = f_2 = \phi_2 \kappa_2 = \kappa_2$ ,

from which it follows that:

$$v_{\rm A} = i u_a / \kappa$$

and a measurement of the specific conductance of the advancing sol column, together with the velocity of the rising boundary, provides all the information required. Any form of apparatus provided with suitably placed "Mukherjee side tubes" would be suitable for use in this manner; it is probable, in fact, that many measurements made with the original Mukherjee apparatus could be recalculated in accordance with the above equation.

Equation (II) shows that, apart from the effects discussed above, the concentration of BC in the supernatant liquid is without influence on the value of  $u_{\rm KA}$ . Electrolyte additions to the supernatant liquid are therefore immaterial provided they supply those ions, and only those, which are present in the intermicellar liquid. The addition of other ions may seriously affect the result. This point is illustrated by the experiments we have performed with different supernatant liquids. The addition of small quantities of sodium citrate to the ultrafiltrate made no significant difference to the measurements made in series L (series I is irrelevant as the sol had aged appreciably between the two groups of measurements). On the other hand, a supernatant liquid consisting solely of sodium citrate gave quite different results (series K and L), indicating, as we have already suggested, that the inter-

micellar liquid contains both citrate and hydroxyl ions, whose ratio will not be much affected by small additions of citrate, but is seriously disturbed by the addition of relatively large quantities. Finally, the use of silver hydroxide in the supernatant liquid completely altered the behaviour of the system by introducing a new ion.<sup>17</sup> These considerations indicate that extreme caution must be observed in the use of "artificial" supernatant liquids, and suggest that ultrafiltrate is the only suitable liquid to employ with sols the composition of whose intermicellar liquid is unknown.

## 5. Summary.

Experimental investigations have been made of the transport and the moving boundary methods of measuring the cataphoretic mobility of a colloidal micelle, and the results of the two methods have been compared. A precision of about 3 per cent. has been obtained in the transport method, and, in favourable cases, a slightly higher precision in the moving boundary method.

Reasons are given for supposing that the results of the transport

method are substantially correct.

The Kohlrausch-Weber theory of ionic displacements has been applied to the moving boundary method of cataphoresis, and it is inferred that the usual interpretation of experiments by this method is erroneous. Methods of experiment and calculation are, however, indicated by means of which correct results may be obtained by the moving boundary technique, and some conclusions are drawn as to the selection of a suitable supernatant liquid.

Our best thanks are due to Mr. A. F. Core for valuable help and advice in the mathematical portions of the paper; to Professor Arthur Lapworth for his continued interest and advice; to Mr. M. G. Evans for helpful criticisms of the draft manuscript; to the Department of Scientific and Industrial Research for a maintenance grant to one of us; and to Messrs. Imperial Chemical Industries, Limited, a grant from whom has defrayed part of the cost of the apparatus.

The Thomas Graham Colloid Research Laboratory, The Victoria University of Manchester.

<sup>17</sup> Neither the ultrafiltrate nor the liquid remaining after coagulation of the sol with sodium sulphate showed any detectable trace of silver ions.

#### REVIEWS OF BOOKS.

Atmospheric Electricity. By B. F. J. SCHONLAND. (Methuen's Monographs on Physical Subjects.) (London: Methuen & Co., Ltd. Fcp. 8vo. Pp. 100. Price 2s. 6d. net.)

This small book is an excellent introduction to a fairly modern subject. It is only since the discovery, by Elster and Geitel and C. T. R. Wilson, of the positive and negative carriers of electricity in the atmosphere that the modern theories underlying thunderstorms began to take shape. The author gives a lucid account of the great developments from both the theoretic and the experimental sides which have since taken place. The chapters are entitled: (i) the ionisation of the

atmosphere, (ii) the penetrating radiation, electric fields and electric currents in the atmosphere, (iii) the electrification of thunderstorms. He concludes with an excellent summary of the rival theories of C. T. R. Wilson and G. C. Simpson on the charge-distribution in a thunderstorm but is unable to give a definite decision on the strength of their claims. "It is not impossible that both the Simpson and the Wilson mechanism may be at work in a thunderstorm at one and the same time."

Gas Analysis by Measurement of Thermal Conductivity. By H. A. DAYNES, D.Sc., F.Inst.P. (Cambridge: The University Press, 1933. Pp. viii + 357 with 76 diagrams. Price 16s.)

This book is an authoritative survey of the theory and technique employed in the analysis of gases by the thermal conductivity method. The author has had a wide experience of academic and industrial research in this field and has access to material which is not available to many persons.

The scientific basis of the method is set out in the first twelve chapters and in three appendices. The thermal conductivity of gases and gaseous mixtures, the theory of the hot wire conductivity bridge, the use of different types of resistance bridges and meters, and the behaviour of the various types of apparatus in practice, form the main content of this section. The information which is made available will prove of very great value for those who desire either to work out for themselves new methods of analysis or who are interested in problems involving the use of a heated wire. The methods are applicable to a large number of physical and chemical problems as is pointed out by the author in the last chapter of his book.

The very extensive use to which this method has been put for the control of industrial processes has led to the development of a highly specialised technique for the analysis of simple mixtures of gases and for the detection of abnormal variations in the composition of industrial gases. A large number of gas meters have been designed in connection with the special needs of the different industries, and are available for the control of many large scale operations. The general principles of these methods are adequately discussed by the author in the last half of his book. Boiler-flue and other exhaust gases, fuel gases, the gas from liquid air, the use of conductivity methods in the fixation of atmospheric nitrogen and the application of the methods to aeronautics are dealt with in detail. There are many problems yet unsolved, especially in the case of fuel gases, and the method has not yet been successfully applied to the analysis of very complex mixtures which have a variable composition. The success which has already been attained leads one to hope that such problems will not prove intractable.

W. E. G.

# INVESTIGATION OF THE CORROSION OF IRON, BY ELECTRON DIFFRACTION.

By J. Cates, A.R.C.S., B.Sc.

Received 20th March, 1933.

This research is a development of one of Professor G. P. Thomson's investigations of surface layers by electron diffraction.<sup>1</sup> The apparatus used was similar to that employed by Professor Thomson. The energy of the electrons used was in the neighbourhood of 30,000 volts and they were generated in a discharge tube, using an induction coil and a rectifying valve. The specimen was in the form of a block of which the surface to be examined was about I cm. square. When the surface is polycrystalline the diffracted electrons form a system of semi-circular rings on a photographic plate which is 40 cm. distant from the specimen in this apparatus.

#### Experimental.

The surface of the specimen to be examined was ground with emery paper of varying grades and then polished, after which the specimen was cleaned in alcohol and distilled water or caustic potash and distilled water.

Several methods of rusting were used and different kinds of iron and steel were examined. These consisted of Swedish iron, ordinary soft iron, a hard cast steel, a nickel steel (Ni 3·4 per cent.) and a manganese steel (Mn 0·9 per cent.). The method of rusting chiefly used, was to place the specimen flat on the bottom of a vessel filled with distilled water to a depth of a few inches and open to the air. In a few cases the rate of rusting was increased by bubbling air through the water. Most specimens were examined when they were covered with a fairly uniform coating which was obtained in a day or two when no air was bubbled through the water, but in a few hours when this was done. The rust generally gave quite good patterns.

The rust was practically always yellow or yellow-brown; in a few cases, however, it was black. This was obtained on some steel blades which were rusted in fairly deep water, lying flat on the bottom of the vessel.

The diffraction pattern given by the rust was in the main the same in all cases, including the black rust. In one or two cases, a few extra lines were obtained indicating the presence of additional material.

#### Results.

The results obtained with different specimens are given in Table I.

TABLE I:—Spacings of the Diffracton Patterns of Rust given by Various Specimens.

Swedish Iron. (7 Plates).	Cast Steel and Steel Blade. (4 Plates).	Nickel Steel. (2 Plates).	Manganese Steel. (3 Plates).	Steel in KCl. (2 Plates).	Black Rust. (r Plate).	Scraped Rust. (2 Plates).	Average.	Professor Thomson's Results.
5 spot 3·26 2·99 2·44 2·33}2·39	6 spot 3·11 — 2·33	3·15 	3·16 - 2·37	3.13	3·25 - 2·36	3·19  2·39	5·5 spot. 3·19 f.s. 2·95 w. 2·36 s.	3·15 (2·79) 2·43 2·22
1.85 1.85 1.70 1.60 1.50 1.41 1.36 1.24 1.18	1.87 1.81 1.68 1.47 1.34 1.15	1·84 1·68 1·47 1·34 1·16	1·86 1·70 1·47 1·34 1·16	1·86 1·67 1·47 1·33 1·16	1.88 1.68 	1·86 1·67 ————————————————————————————————————	1·87 (1·83 f. 1·69 f. 1·59 w. 1·48 v.s. [1·40] 1·35 s. 1·23 w. 1·16 f.s.	1.93 1.84 1.64 

The number of plates from which the average has been obtained in each case is given in each column. The spacings are given in A.U.

Letters used in describing the intensities are: v.s., very strong; s., strong; f.s., fairly strong; f., fair; w., weak.

The general appearance of all the spectra is the same, but in order to compare them accurately, one rather good plate, Plate II. (Swedish iron) was regarded as standard and the others compared with it. If two spectra are obtained with rays of different wave-length, but given by the same substance, the ratio of the radii of corresponding rings is constant for all the rings. This was found to be the case for all the rust spectra.

The radii of the rings on the standard plate were checked on a photometer. The average of all the spectra is given. In the last column of Table I. are given the results obtained by Professor Thomson, which are seen to be in good agreement.

The Swedish iron specimens and all the steel specimens were rusted in distilled water. No air was bubbled through the water in the case of the Swedish iron, but this was done in the case of all the steels except for the steel blade whose spectrum is included in the cast-steel results.

The spacings of the patterns obtained with the Swedish iron specimens are given in Table II.

 $\tilde{A}$  steel blade was rusted in N/50 KCl solution. In this case the blade was placed in a vertical position at the top of the liquid.

Scraped Rust.—Two steel specimens were scraped with a razor, removing the yellow layer and revealing the black lower layer which is usually present in rust. Surprisingly, but similarly to black rust, this under layer gave exactly the same pattern as the yellow top layer.

TABLE II.—Spacings of Patterns obtained with Swedish Iron Specimens	
(The voltages are given in K-volts.)	

Plate Number 11.	5•	7.	9.	10.	12.	13.	Average.
Voltage 35.6.	37*8.	42.2.	33.1.	28.5.	19.6.	24*8.	
3.24 f. s. 3.01 v.w. 2.44 s. 2.33 s. 2.07 w. 1.88 f.s. 1.80 f. 1.69 f. 1.58 w. 1.49 v.s. 1.34 s. 1.23 w. 1.16 s.	3·35 2·38 — 1·91 1·86 1·73 — 1·53 — 1·18	3·10 2·35 2·00 1·85 1·68 1·47 1·38 1·33	2·43 2·04 1·91 1·87 1·71 1·64 1·50 1·44 1·36 1·25 1·18	2·38 	3·34 2·49 — 1·97 — 1·53 — 1·40 —	5 3·25 2·96 2·40 2·03 \$1·90 \$1·83 1·71 	5 3·26 2·99 2·39 2·02 1·91 1·85 1·70 1·60 1·50 1·41 1·36 1·24 1·18

#### Discussion of Results.

The average spacings have been deduced from the measurement of twenty-one plates. The spectra on the whole are fairly good. The difference in the spacings does not amount to more than 7 per cent. or 8 per cent., which is within the errors in measurement. Since the spectrum is practically the same in all cases, and obtained under a variety of conditions, it is most likely due to a single substance. The exception to this is the extra line of spacing I·4I obtained with Swedish iron specimens, and the intensity of which is not the same on the two plates on which it appears. It is thus most likely due to an additional substance. Of the weaker lines of the rust pattern, that at 2·03 spacing can be distinguished in a number of plates, while the 2·95, I·59 and I·23 spacings can be distinguished only on a few plates with Swedish iron.

The resolution of the 1.89 and 1.83 spacings is definite on a number of plates.

On a few plates (one Swedish iron, two cast steel) there is a single strong spot of about spacing 5. There seems to be no indication of a complete ring on any of the plates on which it appears. All these three plates, however, are marked with spots due to the presence of fairly large crystal lumps, and it might be that the ring corresponding to this strong spot of large spacing is too weak to appear, but that the spot is given by a crystal lump suitably placed.

## Consideration of the Oxides and Hydroxides of Iron.

Ferric Oxide exists in two forms, the  $\alpha$  and the  $\gamma$  forms.<sup>2</sup> The  $\alpha$ -modification, which is the more stable, is non-magnetic and has a crystal structure of which the unit cell is a rhombohedron. The less stable  $\gamma$ -modification is ferromagnetic like Fe<sub>3</sub>O<sub>4</sub> and has a crystal structure

<sup>&</sup>lt;sup>2</sup> Welo and Bandisch, Phil. Mag., 50, 399, 1925.

which is indistinguishable crystallographically from Fe<sub>3</sub>O<sub>4</sub>. It may

be prepared by heating Fe<sub>3</sub>O<sub>4</sub> in air at about 220° C.

Ferric Hydroxide. — Corresponding to these oxides there are the α- and γ-ferric hydroxides.<sup>3</sup> Both these hydroxides are yellow when powdered, and have similar though distinguishable crystal structures. They are both paramagnetic and have about the same susceptibility. Both decompose when heated at about 220° C. for a few hours into the corresponding oxides which differ greatly in magnetic properties. These are the only hydroxides of iron known other than ferrous hydroxide. The mineral forms of the hydroxides are Goethite ( $\alpha$ ) and Rubinglimmer

The preparation and difference between these hydroxides has been studied by G. Schikorr.4 Other possible constituents of rust are Fe<sub>3</sub>O<sub>4</sub>, which forms no hydroxide, and the green intercombinations of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, about which little is known. Ferrous hydroxide would not

be expected to be present in the outer layers of rust.

The crystalline ferric hydroxides would be expected to form the chief constituents of rust.

### Previous Analysis of Rust.

X-ray analysis of rust has been carried out by F. Drexler, who examined the rust formed by atmospheric corrosion. He found it to consist in the main of  $\gamma$ -FeOOH together with small traces of  $\alpha$ -FeOOH and Fe<sub>3</sub>O<sub>4</sub>. C. Carius 6 examined rust formed in distilled water of varying acidity and found that in feebly acid water the rust was mainly γ-FeOOH together with a small amount of Fe<sub>3</sub>O<sub>4</sub>, the proportion of γ-FeOOH increasing with the acidity. In alkaline water he found traces of a hydroxide as yet unidentified.

#### Identification of Rust with $\gamma$ =FeOOH.

Rust has been identified with y-FeOOH by obtaining the diffraction pattern of this substance in the form of the mineral Rubinglimmer.

Further, since, on heating, y-FeOOH changes into y-Fe,O, the rust was heated for a few hours at 220° C. in air, after which it gave a pattern which has been identified with y-Fe<sub>2</sub>O<sub>3</sub>. Rubinglimmer heated in a similar way gave practically the same pattern. This pattern is quite different from that of ordinary unheated rust.

In addition to this definite identification a yellow hydroxide of iron was prepared by slow oxidation of Fe(OH)<sub>2</sub> (G. Schikorr 4) and was found to give the same pattern as rust and to behave similarly on heating.

The rust spectrum has also been compared with the X-ray spectrum of  $\gamma$ -FeOOH in the form of Rubinglimmer.

In the course of the work the diffraction patterns of  $\alpha$ -FeOOH

(Goethite), heated α-FeOOH, and Fe<sub>3</sub>O<sub>4</sub> have also been obtained.

All the substances were examined by putting them as a thin layer of powder on a metal block. The substances were cleansed in alcohol and distilled water before powdering up, and they were put on the block

<sup>3</sup> Herroun and Wilson, Proc. Physic. Soc., 41, 100, 1928.

<sup>&</sup>lt;sup>4</sup> Z. anorg. Chem., **191**, 322, 1930. <sup>5</sup> Korrosion und Metallschutz, Jan., 1930.

<sup>6</sup> Z. anorg. Chem., 197, 254, 1931.

as a thin layer of paste. After drying, the powder surface was lightly scraped with a razor to make it flat and fairly smooth. The patterns obtained by this method were not, however, so good as those given by naturally formed surfaces or etched metal surfaces.

Heating the powder *in situ* did not improve the patterns very much, although in the case of most of the substances examined here, they could not be heated above 200° without transformation taking place.

#### Results.

In Table III. the diffraction patterns of Rubinglimmer, the artificially prepared yellow hydroxides, and Goethite are given with the rust pattern. The X-ray patterns of Rubinglimmer and Goethite are also given. The Rubinglimmer and Goethite were powdered whilst moist and examined on copper blocks.

There is seen to be very good agreement between Rust and Rubinglimmer. There are small differences which are considered further on.

The spectrum of Goethite is seen to be essentially different from rust. The yellow hydroxides were prepared from the precipitate obtained on adding ammonia to ferrous sulphate. The liquid was allowed to stand open to the air for a few days after which the yellow layer formed on top was removed, and some of it examined. This hydroxide is denoted by (a). A similar hydroxide (b) was obtained when the liquid was shaken up in a flask leaving a sediment on the walls which quickly turned to yellow hydroxide.

The patterns obtained with these substances are only slightly different from one another and agree well with the rust pattern.

TABLE III.—Spacings of the Diffraction Patterns given by various Hydroxides of Iron Investigated.

Rust.	Rubin- glimmer.	Yellow Hydroxide. (a).	Yellow Hydroxide. (b).	Goethite.	Rubinglimmer X-rays.	Goethite X-rays.
5.5 spot	5 spot			_	{6·4 \ f.s. {5·8 \ s.	4.04 f.s.
3·19 f.s.	3·30 f.s.	3·17 f.s.	3·19 f.s.		3·20 f.s.	3.75 f.s. 3.30 w.
2·95 w.				_	$F {2.93 \text{ w.} \atop 2.62 \text{ w.}} 2.71 \text{ wB.}$	2·95 w.
2·36 s.	2·49 s.	2·35 s.	2·36 s.	2·40 s.	2·41 s.	2.62 s. 2.39 s.
2·03 w.	2.20 w.	2·05 w.	2·10 w.	2·15 f.s.	2·05 f.s.	2·20 f. 2·12 f.s.
$\begin{bmatrix} 1.88 \\ 1.83 \end{bmatrix}$ f.s.	1·90 w.	1.85 f.s.	1∙86 w.		∫1·91 s. 1·84 wB.	1.87 f.
1·69 f.	1·70 f.	1.67 w.	1.68 f.	1.70 s.	1.71 f.s.	1·69 s.
1·59 w.			_	1·55 1·50}w.		
1·48 v.s.	1·48 s.	1·46 s.	I-47 S.		$F_{1.52 \text{ w. } 1.51 \text{ s.}}^{1.56 \text{ s.}} B$	{1·58 f.s. 1·54 s.
[1.40]	-		_	-	1·42 f.	1.49 f.s.
1·35 s.	1·37 f.	1·32 f.s.	1.33 f.s.	_	1·35 f.s.	∫ 1·44 s. \ 1·34 f.s.
1·16 f.s.	1·19 s.	1·19 f.s.	1·16 f.s.		1·19 s.	1.29 f. 1.12 f.s.

The X-ray spacings of Rubinglimmer and Goethite were obtained from our own measurements of published diagrams and photographs, this being necessary as there are no actual figures for the spacings published. G. Frebold 7 gives diagrams of the X-ray spectra of  $\alpha$ - and  $\gamma$ -FeOOH and of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. From a knowledge of the X-ray spectrum of the latter the spacings of the chief lines of the other two have been deduced.

The spacings have also been obtained in the same way from the photographs given by J. Böhm.<sup>8</sup> Böhm's and Frebold's results agree fairly well, but in a few places there is a little difference and this has been indicated in Table III. by F = Frebold and  $B = B\"{o}hm$ .

### Heated Rust and Heated Rubinglimmer and Goethite.

These substances were heated *in situ* on metal blocks. After heating for a few hours at 220° C. they all changed colour to red, and while rust and Rubinglimmer were now ferromagnetic, Goethite was not (cf. G. Schikorr<sup>4</sup>).

The diffraction patterns obtained with the heated substances were fairly good. Those given by heated rust and Rubinglimmer are given in Table IV. together with the theoretical spectrum of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, while the ratios of the theoretical spacings to the corresponding spacings in each pattern are given in each column, and are seen to be approximately constant. Heated rust and heated Rubinglimmer differ only slightly.

TABLE	IV.—Spacings	OF	THE	PATTERNS	GIVEN	$\mathbf{B}\mathbf{Y}$	HEATED	Rust	AND
		HE.	ATED	RUBINGLI	MMER.				

Heated Rust.	Ratio Calculated/exptal.	Heated Rubinglimmer.	Ratio Calculated/exptal.	γ-Fe <sub>2</sub> O <sub>3</sub> Calculated.
2·83 f.	1.05		_	2·97 f.
2.40 S.	1.05	2.45 S.	1.03	2.53 s.
2.00 f.	1.04	2.08 f.	1.01	2·11 f.
1·83 w.	1.04	1·83 w.	1.04	(1·91) w.
				1.72 w.
1·54 f.	1.04	1·60 f.	1.01	1.61 f.
I·43 S.	1.04	1.43 s.	1.04	1·49 s.
			-	1.27 W.

The theoretical spectrum of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, is actually that of theoretical Fe<sub>3</sub>O<sub>4</sub> with which, according to X-ray analysis, it is almost identical. The spectrum was calculated using the Thomas-Fermi formula for atomic scattering factors.

Heated Goethite gave a pattern which differed from heated rust and Rubinglimmer but was the same as  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

The yellow hydroxides when heated were ferro-magnetic and gave the pattern of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

#### Comparison of Rust and Rubinglimmer Patterns.

Although the rust and Rubinglimmer patterns agree quite well, Table III., in two respects they are in disagreement.

<sup>7</sup> Metall. u. Erz, 23, 115, 1926.

<sup>8</sup> Z. anorg. Chem., 143, 115, 1926.

Whilst in the Rubinglimmer pattern the 1.90 spacing is slightly weaker than the 1.70 line spacing, in the rust pattern the corresponding 1.87 line (resolved as double in a few cases) is definitely stronger than the 1.69 line. Also, the 2.20 spacing in Rubinglimmer is relatively larger than the corresponding 2.03 spacing in rust, and appears relatively stronger in Rubinglimmer. The yellow hydroxides (a) and (b) differ in the same way.

In the case of the heated substances, Table IV., the chief differences are that the I.83 and I.43 spacing are relatively larger, in the rust

pattern.

These differences may be due to the presence of α-FeOOH in Rubinglimmer. From a consideration of the spectra of Rubinglimmer, rust and Goethite, it is seen that the presence of α-FeOOH in either Rubinglimmer or rust would tend to make the 2·20 spacing larger and relatively stronger, and the I·70 spacing relatively stronger, which is the way in which the rust and Rubinglimmer spectra differ.

Also in the case of the heated substances, from a comparison of the theoretical spectra of  $\alpha$ - and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> given below, it is seen that the presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> would tend to make the weak I·9I ring rather larger in radius than in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> alone, and also to bring the next ring (I·60 spacing) closer to the centre, which is similar to the difference between the heated rust and heated Rubinglimmer.

TABLE V.—Comparison between the Theoretical Spectra of  $\alpha\textsubscript{-}$  and  $\gamma\textsubscript{-} Fe_2O_3.$ 

The possible presence of  $\alpha$ -FeOOH in Rubinglimmer might be due to impurities or might be brought about by partial transformation of Rubinglimmer on powdering.

A comparison between the rust pattern and the theoretical  $Fe_3O_4$  pattern shows that the presence of the latter substance would not account for the observed differences between Rust and Rubinglimmer.

## Examination of Fe<sub>3</sub>O<sub>4</sub>.

This was prepared by Haber's method <sup>8</sup> and was examined on copper and iron blocks. The diffraction pattern obtained could not be associated with the theoretical pattern and was different from heated rust and heated Rubinglimmer. The surprising thing was that it was similar to rust. The pattern obtained is given in Table VI. together with that of rust and  $Fe_3O_4$  theoretical, and it is seen to differ from rust in the same way as does Rubinglimmer, although one pattern was more like rust. This would indicate that there is a thin invisible layer of  $\gamma$ -FeOOH on  $Fe_3O_4$ .

When the  $Fe_3O_4$  was powdered on iron the rings obtained were at first poor, but when the specimen was examined, after a few weeks (after lightly rescraping it) the patterns were much better. It was

<sup>8</sup> Welo and Baudisch, Phil. Mag., 3, 396, 1927.

Fe <sub>3</sub> O <sub>4</sub> Obtained.	Fe <sub>3</sub> O <sub>4</sub> Calculated.	Rust.
3·13 f. s. 2·35 s. 2·12 W.	2·97 f.s. 2·53 s. 2·11 f. ((I·91) w.)	3.19 f.s. 2.36 s. 2.03 w.
1·84 W. 1·65 f. 1·46 s.	1·72 w.) 1·61 f. 1·49 s.	1·87 f. 1·69 w. 1·48 s.
1·32 f.s. 1·16 w.	1·27 w.	1·35 f.s. 1·16 f.

TABLE VI.—Spacings of the Pattern given by Fe<sub>3</sub>O<sub>4</sub>.

indeed noticed that there were a few yellow spots on the specimen which was, however, black as a whole.

These results may be considered together with the fact that the black under-layers of rust and black rust also gave the usual rust pattern.

#### Summary.

The rust formed on iron and steel specimens has been examined by electron diffraction. Although different kinds of iron and steel, and different methods of rusting were tried, the diffraction pattern was always the same.

This pattern has been identified with  $\gamma$ -FeOOH, the electron diffraction pattern of which (in the mineral form Rubinglimmer) has been obtained. On heating, rust changes into ferromagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and the diffraction pattern of heated rust has been identified with  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. The small differences between the patterns of rust and Rubinglimmer, and between these heated substances, have been shown to be possibly due to the presence of a little  $\alpha$ -FeOOH in the Rubinglimmer.

The diffraction pattern given by  $\text{Fe}_3\text{O}_4$  (chemically prepared) could not be associated with the theoretical  $\text{Fe}_3\text{O}_4$  pattern, but instead it was almost the same as the rust pattern, indicating that a thin layer of  $\gamma$ -FeOOH was present on the  $\text{Fe}_3\text{O}_4$ .

I have great pleasure in thanking Professor G. P. Thomson, who suggested the research, for his help and encouragement in this investigation. I also desire to record how very much I appreciate the help which I received from Mr. C. R. Ensor, B.Sc., Lecturer in Physics, and from Mr. R. W. B. Stephens, B.Sc., Assistant Lecturer, together with whom the apparatus was set up, and a start made on the actual investigation of iron rust.

I also wish to thank the Royal School of Mines for supplying me with samples of steels and with mineral Goethite.

#### THE NATURE OF SPONGY ZINC DEPOSITS. BY THE ELECTROLYSIS OBTAINED AQUEOUS SOLUTIONS OF ZINC SULPHATE.

By W. S. Sebborn, B.Sc., A.I.C.

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Various and conflicting theories have been advanced concerning the nature and causes of the formation of sponge during the electrolytic deposition of zinc. Mylius and Fromm 1 regard spongy zinc as zinc disturbed in crystallisation by absorption of oxygen, with subsequent formation of zinc oxide; a similar theory was put forward by Nahnsen.<sup>2</sup> Siemens and Halske 3 regard the phenomenon as being due to the formation of zinc hydride, which exerts an unfavourable influence on the deposited zinc. Foerster and Günther 4 consider sponge formation to be due to the presence of zinc hydroxide or basic zinc salts in the deposit, formed by the reaction between the feebly basigenic zinc and water, which hinder the crystallisation of the zinc. Research, however, appears to have been directed towards the technical problems of the prevention of sponge formation during metal deposition, and to the preparation of zinc dust, from spongy zinc deposits, for reduction reactions, rather than towards an explanation of the phenomena concerned.

The following paper describes experiments which have been carried out in investigation of the formation of spongy zinc deposits by the electrolysis of aqueous solutions of zinc sulphate.

#### Experimental.

#### The Dependence of Sponge Formation on Concentration of Solution and Current Density.

For these experiments, aqueous solutions of zinc sulphate were electrolysed under varying conditions of current density. All electrolyses were conducted at a temperature of 20° C. The electrodes used were of rolled sheet electrolytic zinc, and were maintained in a vertical position throughout electrolysis. The zinc sulphate employed was of A.R. quality, obtained from British Drug Houses.

In each case, electrolysis was allowed to proceed for about five minutes, after which the cathode was removed from the solution, and the deposit examined. As the current density increased, the character of the deposit passed through a series of successive stages. With low current density,

Siemens and Halske, D.R.P., 162785, 1905.
 Foerster and Günther, Z. Elektrochem., 5, 20, 1898; Foerster, "Elektrochemie

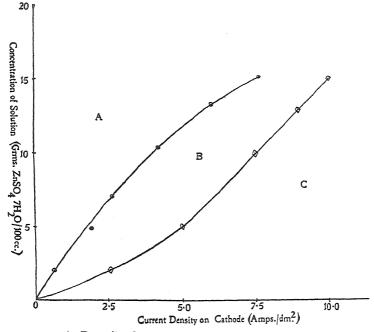
<sup>6</sup> Morgan and Ralston, Trans. Amer. Electrochem. Soc., 30, 229, 1916; D.R.P., 276984, 1913; Chemische Fabrik Griesheim-Elektron.

<sup>&</sup>lt;sup>1</sup> Mylius and Fromm, Z. anorg. Chem., **9**, 164, 1895. <sup>2</sup> Nahnsen, Berg und Hüttenm. Ztg., p. 393, 1893.

wässeriger Lösungen," p. 484, 1915.

5 Sherard Cowper Coles, B.P., 13977, 1907; Schnabel and Louis, Handbook of Metallurgy, vol. ii.; Foerster, Electrochemie wässeriger Lösungen, p. 485, 1915; J. W. Mellor, Theoretical and Inorganic Chemistry, vol. iv., pp. 416, 417.

the deposit was coherent, and adhered well to the electrode: as the current density was increased, the deposit darkened in colour, becoming semi-crystalline, and non-adherent, and finally, when high current-densities were employed, it consisted of black, voluminous sponge. It was found possible to determine approximately, for each concentration of zinc sulphate studied, two critical points in the transition of the deposit from the coherent to the spongy condition: the lowest current density at which the deposit could be readily removed from the cathode by gentle rubbing with the finger, and that at which definite black sponge formation was first observed. These two points were obtained for each concentration studied, and were plotted as abscissæ with concentration of solution as ordinates. The effective areas of the anodes and cathodes in these experiments were each



- A. Deposit coherent.
- B. Deposit loose, non-adherent, semi-crystalline.
- C. Deposit spongy.

Fig. 1.—Relation between character of deposit, concentration of solution and current density at 20° C.

9.9 sq. cms. By connecting corresponding points, two curves were obtained, representing the first appearance of a non-adherent deposit (curve A, Fig. 1), and the first appearance of definite sponge (curve B, Fig. 1). The resulting diagram gives an indication of the relationship between the formation of sponge, the concentration of the solution, and the current density on the cathode.

It will be seen from the graph (Fig. 1) that the current required to produce spongy zinc at vertical cathodes is approximately proportional to the original concentration of the solution. This is in accordance with what would be expected, if natural convection in the liquid supplies fresh ions to the cathode just in the time necessary to reduce their con-

centration to zero, from the formula for calculating the diffusion coefficient given by Sand,7

 $K = \frac{1 \cdot 1284^2}{96540^2} \, \frac{i^2 t n_a^2}{C^2}$ (I)

where  $K = \text{diffusion coefficient (cm.}^2/\text{sec.})$ .

 $n_a = \text{transport value of anion.}$ 

C = concentration of solution (mg. equivs./c.c.).

 $i = \text{current strength (milliamps./cm.}^{2}$ ).

Capillary

Electrometer

t =time in seconds for concentration of metal ions at cathode to reach zero.

It would also hold for a vigorously stirred electrolyte having a diffusion layer of definite thickness, as envisaged by Nernst and Brunner.

Electrode-The position of Zinc from Zinc Sulphate Soluthe tions, on Lower Surface of a Horizontal Cathode.

The apparatus used in these experiments was a slight modification of that for the study of electrolysis in perfectly stationary

liquids, described by Sand,7 and is shown diagrammatically in Fig. 2.

The brass cathode C was clamped over a central hole in the perfectly flat glass plate D, forming an airtight joint on the flanged glass cylinder H. The cathode and clamp were held in position by the screws  $s_1$  and  $s_2$ , elastic pressure being maintained by means of small pieces of solid rubber W<sub>1</sub> and W<sub>2</sub>. The thick walled glass tube R, one end of which was bevelled, was clamped centrally to the flanged cylinder H, so that the bevelled end exactly covered the central hole in D, and was also held in position by the rubber bung B<sub>1</sub>, carrying a glass connection X1 to the auxiliary The other calomel electrode E.

H Zine Anode FIG. 2.

end of R passed through a second rubber bung B2, which connected it to a short glass cylinder J, serving as the anode compartment. This was

<sup>7</sup> Sand, Trans. Far. Soc., I, I.

closed at its other end by a third rubber bung, B<sub>3</sub>, carrying connections for the anode (a disc of pure sheet zinc), a vent F, and the filling tube G.

The experimental procedure was as follows: The whole apparatus was inverted, and filled, through G, with the solution under investigation, care being taken to expel all air bubbles. The apparatus was then set up in position, with the cathode uppermost, and the cathode adjusted to horizontal by means of a small spirit level, placed on D. The electrical connections were made, as shown in the diagram. The potential difference between the cathode and the auxiliary (saturated calomel) electrode E, was measured, on the potentiometer circuit shown, continuously throughout the experiment, the time of electrolysis being measured by means of a stop watch. The current flowing from anode to cathode was kept constant, and measured by the milliammeter (A). At the same time, visual observation of the lower surface of the cathode was accomplished, with the aid of a mirror placed at M. The variation of the potential difference between the auxiliary electrode and the cathode, was plotted against the time. The curve obtained showed a sudden rise at the point where the solution became depleted of metal ions in the neighbourhood of the cathode, and greatly increased polarisation occurred.

In later experiments, the potentiometer was dispensed with, and a high resistance millivoltmeter (50,000 ohms) substituted, the only observation taken being the time which elapsed between the switching on of the current and the sudden sharp change in potential.

If the sudden increased polarisation is due to depletion of metal ions at the cathode, then, from equation (I) if  $n_a$  and K be assumed constant,  $i^2t$  is constant for a given solution, and  $\frac{i^2t}{C^2}$  is constant, independent of the concentration.

The results obtained are shown in the Table; the effective area of cathode being 0.79 cm.<sup>2</sup>.

Concentration of Solution gms. ZnSO <sub>47</sub> H <sub>2</sub> O per 100 c.c.	Current Density on Cathode (i).	Time $(t)$ secs.	i <sup>2</sup> t.	$rac{i^2t}{C^2}$ (Mean).
I I	1·27 2·53 3·80	150 35 15	240·5 224·4 216·2	227
2·5	1·27	965	1547	248
2·5	2·53	241	1545	
2·5	3·80	102	1470	
2·5	5·06	62	1590	
2·5	6·33	40	1603	
2·5	7·60	27	1557	
5	2·53	975	6248	253
5	5·06	240	6155	
5	6·33	168	6728	
5	7·60	112	6460	
5	12·66	38	6092	

Experiments were also carried out, using current densities so high that depletion of the solution in zinc ions, in the neighbourhood of the cathode, took place immediately, with instant polarisation.

In no case, either with the higher or the lower current densities, was it found possible to obtain a spongy deposit. A bubble of gas was, in

all cases, formed, which hindered deposition of zinc on the cathode. The surface of the bubble was coated with zinc hydroxide, and the deposit was, for the most part, bright and coherent: a slight tendency to sponginess was noticed at the edges, where the edge of the bubble met the cathode (see Fig. 3).

# The Chemical Analysis of Spongy Zinc Deposits.

Spongy deposits were obtained by the electrolysis of 2 per cent. aqueous solutions of zinc sulphate, on vertical cathodes, using anode and cathode of electrolytic rolled sheet zinc. The deposit was removed, by means of

C В H S

C. Cathode. B. Bubble H. Zinc hydroxide layer. B. Bubble. S. Solution.

Sponge formation takes place at  $S_1$ ,  $S_2$ . FIG. 3.

a glass rod, into a clean beaker, and was washed rapidly, by decantation, with distilled water, until free from electrolyte. A final wash with alcohol and ether followed, and the deposit was sucked dry in a Gooch crucible, and finally dried in an oven at 60° C. The resulting powder was immediately examined, and was found to consist principally of metallic zinc, contaminated with large amounts of oxide and hydroxide: some basic carbonate and sulphate were also found, but in very small quantities. The total zinc content was determined by weighing the dried deposit into a tared crucible, dissolving in dilute nitric acid, evaporating to dryness on a water bath, and igniting strongly to constant weight, the residue in the crucible being weighed as zinc oxide.

The mean value obtained from nine such determinations was 95.16 per cent. total zinc. This corresponds to a composition of 75-85 per cent. zinc in the metallic state, the remainder being in combination as oxide or hydroxide.

## Inferences from Experiments.

The formation of zinc sponge by electrolysis is linked up with the production of zinc hydroxide at the cathode. When current densities. which, with vertical electrodes, would produce a spongy deposit, are used with horizontal electrodes, and a perfectly still solution, coherent deposits are obtained, the zinc hydroxide being kept from contact with the deposited metal by surface effects of the bubble of hydrogen. It was shown that, where the zinc hydroxide did come into contact with the deposited zinc (at the edges of the bubble, the deposit tended to be spongy.

This is in opposition to the view that the sponginess of zinc depends on hydride formation, and supports the theory advanced by Förster and Günther, that sponge formation is due to formation of zinc hydroxide by reaction of Zn" ions with OH' ions at the cathode, left by migration of H' ions, and subsequent occlusion of the zinc hydroxide in the deposit, retarding crystal growth.

Spongy deposits were found to be favoured, in general, by low concentration of the solution in metal ions, and by the use of high current densities.

In conclusion, the author wishes to express his thanks to Dr. H. Sand, for his interest and advice during the progress of this investigation.

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# THE EFFECT OF HYDROGEN-ION CONCENTRA-TION ON THE RATE OF OXIDATION OF SOLUTIONS OF FERROUS CITRATE.

By J. M. Bryan, Ph.D.

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Received 29th May, 1933.

In studies on the effect of hydrogen-ion concentration on the corrosion of iron in the presence of oxygen, it was noticed that the dissolved iron readily oxidised to the ferric condition in the less acid members of the series but not in those of high acidity. There is little information concerning the effect of hydrogen-ion concentration on the rate of oxidation of ferrous iron in solution, but Baylis states that oxidation may be 100 times as rapid at  $p_{\rm H}$  9.5 as at  $p_{\rm H}$  5.5 and that this may have a high controlling influence on the corrosion of iron. In view of this statement and the conclusion arrived at by Forest, Roetheli and Brown, that the chemical composition of a film of oxide has an important influence on the corrosion of iron and is related to the  $p_{\rm H}$ -value of the liquid near the surface of the metal, it seemed desirable to carry out the present investigation.

Two methods were used in which the conditions of aeration were different. In the first, the oxidation of de-aerated solutions of ferrous citrate was brought about by bubbling air through the solutions at a standard rate; in the second, the oxidation was allowed to proceed under static conditions and in the presence of a limited amount of air.

I. De-aerated solutions having the following composition and hydrogenion concentration were prepared according to the method outlined in a previous paper.<sup>4</sup>

$p_{ m H}$ (by Glass Electrode).	Ferrous Iron	Citric Acid	Sodium Citrate
	(Per Litre).	(Per Litre).	(Per Litre).
3·31 4·66	0·5 gm.	2.5 gm.	0.0 gm.
5·35	o·5 ,,	2·5 ,,	4.5 ,,
5·71		2·5 ,,	15.0 ,,

Fig. 1 illustrates the apparatus with which the aeration was carried out. The bottle (A) of 240 c.c. capacity and containing 180 c.c. of the particular solution to be tested was fitted with two delivery tubes (a and b), by means of which air was bubbled through the solution. A third tube (c), fitted with a rubber connection and clip, provided a means of following the rate of oxidation of the ferrous iron by withdrawing samples of the solution at

1931.

4 J. M. Bryan, Trans. Faraday Soc., 27, 616, 1931.

<sup>&</sup>lt;sup>1</sup> Food Investigation Special Report No. 40, 38, 1931.

<sup>&</sup>lt;sup>2</sup> J. R. Baylis, *J. Ind. Eng. Chem.*, 18, 370, 1926.

<sup>3</sup> H. O. Forest, B. E. Roetheli and R. H. Brown, *J. Ind. Eng. Chem.*, 23, 650,

intervals for titration against a standard solution of titanium chloride. The rate of the passage of air through the solutions was 8 litres per hour,

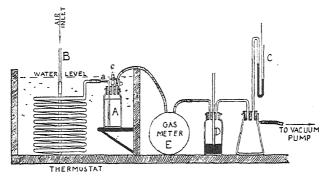


Fig. 1.—Apparatus for bubbling air through solutions of ferrous citrate at a constant rate.

this being regulated partly by the length of fine capillary glass tubing (B) and partly by suction from the vacuum pump. The glass tube dipping under the mercury in bottle (D) was adjusted so that a slow stream of air

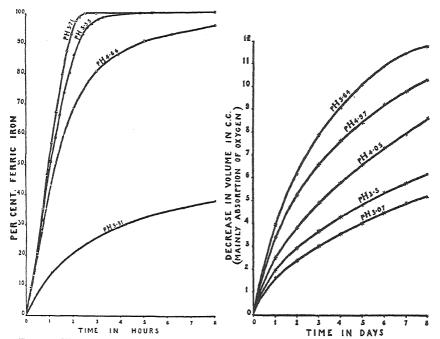


Fig. 2.—The effect of hydrogen-ion concentration on the rate of oxidation of solutions of ferrous citrate.

Fig. 3.—The effect of hydrogen-ion concentration on the absorption of oxygen by solutions containing ferrous citrate.

was drawn into the bottle from outside. This minimised the effect of variations in the suction from the water pump. The manometer (C) served as an indicator in controlling the rate of aeration which was checked occa-

sionally by means of the gas meter (E). The experiment was conducted at a temperature of 25° C., the air used for the aeration of the solutions being raised to this temperature by passing it through the long coil of glass tubing. The solutions were aerated for a period of eight hours, and the results are given by the curves of Fig. 2. These show that oxidation is rapid at  $p_{\rm H}$  5.35 and 5.71 and relatively slow at  $p_{\rm H}$  3.31.

2. De-aerated solutions were prepared as before, but their composition and corresponding hydrogen-ion concentrations were as follows:—

$p_{\rm H}$ (by Glass Electrode).	Ferrous Iron	Citric Acid	Sodium Citrate
	Per Litre.	Per Litre.	Per Litre.
3.07 3.5 4.05 4.97 5.64	o·5 gm. o·5 ,, o·5 ,, o·5 ,,	5.0 gm. 5.0 ,, 5.0 ,, 5.0 ,, 5.0 ,,	o o gm. 1 5 ,, 4 5 ,, 15 0 ,, 40 0 ,,

Bottles of equal capacities (205 c.c.) were completely filled with the deaerated solutions, attached to graduated burettes containing 70 c.c. of air and placed in a thermostat room at 25° C. Thirty c.c. of solution were displaced through the exit tubes of each bottle by pressure of air from the burette, thus distributing the air between the bottles and burettes and improving the conditions for aeration. The experiment was terminated after a period of eight days.

Analysis of the residual gases showed that carbon dioxide was evolved during oxidation and, on this account, the experiment was repeated in duplicate, under biologically sterile conditions, to remove the possibility of any production of this gas through the activity of micro-organisms. Gas analysis (see Table I.) showed that small amounts of carbon dioxide were evolved, as before, particularly in the less acid members of the series. which proves that its presence was due to the breakdown of some oxidation product of the citric acid.

TABLE I.-ANALYSIS OF THE RESIDUAL GASES.

$p_{ m H}$ of Solutions.		Volume of Gas in	c.c. at N.T.P.	
PH of Solutions.	Total.	Carbon Dioxide.	Oxygen.	Nitrogen.
3·07 3·5 4·05 4·97 5·64	57·3 56·3 53·9 52·2 50·9	0·8 0·8 1·6 2·5 2·4	8·5 7·4 4·3 1·7 0·5	48·0 48·1 48·0 48·0 48·0

This evolution of carbon dioxide was very largely balanced by an almost equal absorption of nitrogen, so that the curves shown in Fig. 3 closely represent the progressive absorption of oxygen.

The total absorption of oxygen was found at the end of the experiment by subtracting the residual oxygen, as determined by gas analysis, from that originally present. The results of these determinations are shown by curve A of Fig. 4. The actual volumes of oxygen used in the oxidation of

ferric iron to ferric condition are shown by curve B of Fig. 4, and were found by titrating the solutions against a standard solution of titanium chloride. The difference between these two curves is, of course, due to the secondary or induced oxidation ofthe citric acid, mentioned. already which becomes factor of considerable importance atless acid end of the  $p_{\rm H}$ -range. Both curves would obviously have been steeper if the supply of air had been unlimited as in the previous experiment.

Curves A and B of Fig. 5 are of interest as they illustrate the change in hydrogenion concentration brought about by the oxidation of a ferrous salt in solution. these curves the  $p_H$ values of buffered solutions containing 0.05 per cent. of iron completely in ferrous and ferric conditions, respectively, are plotted against those of similar solutions containing no iron (see dotted curve). In the case of the solutions containing ferric iron it was found necessary to use freshly prepared solutions for the Þн determinations. because slow reduction of ferric iron occurs on standing in the presence of citric acid.

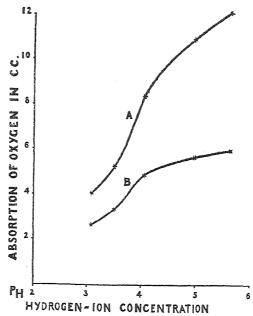


Fig. 4.—The effect of hydrogen-ion concentration on the absorption of oxygen by solutions containing ferrous citrate.

Curve A = Total volume of oxygen absorbed.

Curve B = Volume of oxygen used in oxidising ferrous iron to the ferric condition.

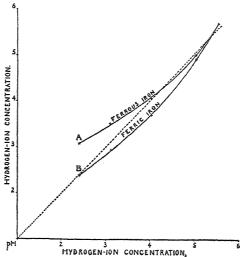


Fig. 5.—Curves comparing the p<sub>H</sub>-values of buffered solutions containing the same amount of iron, as citrate, in the ferrous and ferric conditions.

# THE EXTENT OF DISSOCIATION OF ZINC SULPHATE.

By CECIL W. DAVIES.

Received 29th May, 1933.

In a recent paper under this title Irving A. Cowperthwaite 1 has compared the application of the Gronwall-La Mer theory 2 to zinc sulphate with the writer's treatment of the conductivity data for the same salt.3 However, the activity values he tabulates under the heading "Davies" are quite incorrect, partly because no distinction seems to have been drawn between ion activity coefficients and stoichiometric activity coefficients, and partly through a confusion of equivalent with molar concentrations. For 0.0005 M-zinc sulphate Cowperthwaite gives the following activity coefficients: Observed, 0.780; Davies, 0.831. Actually the conductivity data lead to the figure  $\gamma = 0.771$ , which is obtained as follows. Onsager's equation for zinc sulphate  $\Lambda_x = 113.5 - 287\sqrt{C_i}$ , where  $\Lambda_x$  represents the sum of the mobilities of the zinc and sulphate ions when the equivalent ionic concentration is  $C_i$ . For  $C_i = 0.001$  the equation gives  $\Lambda_x = 104.4$ , whereas the conductivity of the salt is 98.6. If the discrepancy is ascribed to incomplete dissociation a short series of approximations leads to  $C_i$ 0.000942, and combining this with the Debye-Hückel limiting equation gives 0.771 for the stoichiometric activity coefficient. The agreement with experiment is therefore quite good, the remaining discrepancy between the activity and conductivity figures being possibly due to some hydrolysis of the zinc sulphate at high dilutions. The Debye-Hückel equation is here used in place of the empirical modification employed six years ago because in the meantime the difficulties in accepting the Debye-Hückel values have been removed by further work.<sup>4</sup> At higher concentrations than this the limiting equations are no longer valid, so that further comparison is unjustifiable.

It seems unlikely that any decisive test between the two treatments (in so far as they are conflicting) will be reached by considering a single salt in this way. Rather it seems desirable to apply both methods as widely as possible: Gronwall and La Mer's because it is most important to test the underlying theory; and the dissociation-equilibrium treatment because, although it leaves the theoretical question open, it correlates activity and conductivity measurements and can be applied to mixtures as well as simple salt solutions, and thus permits a much wider survey to be made. It is from considering large numbers of salts, when possible in a variety of solvents, that a clarification of ideas concerning ionic solutions is most likely to come. Thus it is interesting to gather from the paper of Cowperthwaite that thallous chloride is

<sup>&</sup>lt;sup>1</sup> Cowperthwaite, Trans. Faraday Soc., 29, 593, 1933. <sup>2</sup> Gronwall, La Mer and Sandved, Physikal. Z., 29, 358, 1928; La Mer,

Gronwall and Greiff, J. Physical Chem., 35, 2245, 1931.

<sup>3</sup> Davies, Trans. Faraday Soc., 23, 351, 1927.

<sup>4</sup> McInnes and Shedlovsky, J. Amer. Chem. Soc., 54, 1429, 1932; Davies, Conductivity of Solutions, 1933, p. 108.

now regarded as incompletely dissociated by workers who do not use this term in its broadest sense. Again, the low, but almost identical, dissociation constants of the bivalent metal sulphates may very well be due to the close approach effect with which Gronwall and La Mer's theory is concerned, but it seems most unlikely that an identical treatment will succeed in interpreting the very different dissociation constants found 5 for the oxalates of the same metals.

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<sup>5</sup> Money and Davies, Trans. Faraday Soc., 28, 609, 1932.

## THE SYSTEM: ANILINE—ACETONE—WATER.

By Alan Newton Campbell and Edith Margaret Brown.

Received 2nd June, 1933.

In the course of some work on the affinity constant of aniline in acetone-water mixtures <sup>1</sup> it became necessary to investigate the 30° isothermal of the above system. Subsequently, the investigation of this system has been completed, since it did not appear to have been studied before.

## Experimental.

Only one pair of the above system, viz., aniline and water, are partially miscible liquids, the other pairs being completely miscible. Addition of acetone to aniline-water mixtures increases the mutual solubility. The details of the 30° isothermal are given elsewhere, but for the sake of completeness, the figures are reproduced here.

	TABLE	I.—Compositions	OF	CONJUGATE	SOLUTIONS	ΑТ	30°.
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Aqueous Layer.				Aniline Lo	ıyer.
	Acetone.	Water.	Aniline.	Acetone.	Water.
Per Cent. ] 3:35 3:81 3:964 4:15 3:85 4:105 4:27 6:1 8:78 12:95 21:1*	Per Cent.  0.0  0.422  0.906  2.64  7.08  9.57  12.78  21.03  25.11  31.56  36.6*	Per Cent. 96·65 95·767 95·13 93·21 89·07 86·325 82·95 72·87 66·11 55·42 42·3*	Per Cent. 95.25 91.5 90.04 83.19 72.66 65.5 59.39 48.32 40.13 28.83 21.1 *	Per Cent. 0.0 3.68 4.509 9.735 5.5 25.15 30.03 37.48 39.45 40.5 36.6 *	Per Cent. 4.75 4.82 5.451 7.075 11.85 9.35 10.58 14.2 20.42 30.67 42.3*

<sup>\*</sup> Critical Composition.

To obtain the complete diagram, or solid model, it is necessary to know the temperature variation of the binary system, aniline-water. According to Seidell's *Dictionary of Solubilities*, aniline and water are completely

<sup>&</sup>lt;sup>1</sup> Campbell and Brown, Trans. Electrochem. Soc., Spring Meeting, 1933.

miscible above 167.7°. This, therefore, is the critical temperature for the system aniline-water, but not necessarily for the system, aniline-acetenewater.

Nine mixtures of acetone, aniline and water, whose total compositions all lay within the heterogeneous area of the 30° isothermal, were made up. These were sealed into hard glass tubes, so that only a small empty space was left for expansion. The tubes were heated, one by one, in a glycerine bath, which was stirred by an electric motor. As the tubes were heated, there was no apparent change, until the temperature approached the temperature of homogeneity. When this temperature region was reached, the solution around the meniscus became decidedly agitated. Heating was continued slowly until finally at a definite temperature the meniscus ceased to be a barrier between the two parts of the solution, and the upper solution poured into the lower one. The bath was kept at this temperature, and in a very short time the two layers had formed one completely homogeneous solution. On cooling slightly, the appearance of turbidity could be very distinctly noted. The mean of these two temperatures was taken as the critical temperature of the mixture in question. The results are given in Table II.

TABLE II.—CRITICAL TEMPERATURES OF MIXTURES.

nposition.		Temperature
Acetone.	Water.	of Homogeneity.
Per Cent.	Per Cent.	
1.4	50∙0	166⋅5° C.
5.0	46.4	156.0
31.68	19.72	104.5
31.68	47.32	86·o
15.84	63.16	122.0
15.84	12.62	92.0
7.92	20.5	136.0
5.0	50∙0	159.0
25·0	45.0	101.0
	Acetone.  Per Cent.  1.4  5.0  31.68  31.68  15.84  15.84  7.92  5.0	Acetone. Water.  Per Cent. Per Cent.  1.4 50.0 5.0 46.4 31.68 19.72 31.68 47.32 15.84 63.16 15.84 12.62 7.92 20.5 5.0 50.0

Knowing the critical temperature and composition of the binary system

Acetone

30°
900

150°
Wate

Fig. 1.—Projection diagram of the solid model representing the temperature variation of the system: aniline—acetone—water.

aniline-water and the temperature of homogeneity of any given ternary mixture, cardboard contours were cut out and erected on the 30° isothermal as a base. The interstices were then filled in with plasticene and a solid model thus constructed. From this solid model the projection diagram given in the figure was constructed.

The curves never lie completely within the triangular area. There is, therefore, no true ternary critical point. The observed critical temperature, 167.7°, is that of the binary system, anilinewater.

# Summary.

I. The system, aniline—acetone—water, has been studied at tempera-

tures between 30° and the binary critical temperature, 167.7°.

2. At constant temperature, the mutual solubility of aniline and water is increased by addition of acetone, in which both aniline and water are readily soluble. The acetone divides itself unequally between the two layers, more entering the layer rich in aniline than the layer rich in water. Therefore, the critical composition is not symmetrically situated on the isothermal.

3. The critical composition at 30° is: 21·1 per cent. aniline, 36·6 per

cent. acetone, 40.3 per cent. water.

4. There is no true ternary critical temperature, the highest temperature at which aniline, acetone and water can form two layers being lower than

the binary critical temperature of aniline and water.

5. Once the basic isothermal is known, the experimental work involved in determining the contour of the solid model is so easy, that this might very well be adopted as an experiment for advanced undergraduate study, in succession to, for instance, the well-known phenol-water system.

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# SURFACE FILMS OF CELLULOSE DERIVATIVES ON WATER AND DYESTUFF SOLUTIONS— PART II.

By J. B. HARDING AND N. K. ADAM.

(From the Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, and Imperial Chemical Industries, Ltd.)

Received 9th June, 1933.

This paper continues the work of one of us <sup>1</sup> on monomolecular films of cellulose derivatives on aqueous solutions; measurements of the "surface potential," or change in contact potential between the solution and air caused by the presence of a surface film are now recorded.

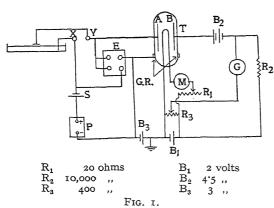
Surface pressure measurements and ultra-microscopic examination of the films were conducted exactly as described in the previous paper on cellulose films; the surface potential was measured nearly as described by us last year,² with two modifications of detail. The brass trough was replaced, in some of the experiments, by a large trough of opaque fused silica of the same internal cross-section, to which the usual instrument for measuring surface pressure could be attached. The silica trough being a non-conductor, the rather inconvenient large sheet of silver, covered with silver chloride, which served as a non-polarisable electrode to connect the liquid in the trough with the potentiometer, could be omitted; a small silver wire covered with silver chloride gave perfectly satisfactory results. The silica trough is also more easily cleaned than the brass trough. Simultaneous measurements of surface pressure and surface potential were made.

<sup>&</sup>lt;sup>1</sup> Trans. Far. Soc., **29**, 90, 1933.

<sup>&</sup>lt;sup>2</sup> Proc. Roy. Soc., 138A, 411, 1932.

The Dolezalek electrometer has now been replaced by an "electrometer triode," 3 used with a circuit substantially the same as that employed by Harrison 4 (Fig. 1). The potential of the air-electrode above the trough is transmitted to one plate A of the triode, by a well-screened and insulated wire through Y; the triode is also screened. The necessary positive potential on plate B is maintained by a 4.5-volt dry battery B2; the galvanometer G measures the current between the filament and plate B. current can be compensated by a variable current through the 10,000 ohm resistance R<sub>2</sub>, controlled by the 400 ohm potentiometer R<sub>3</sub>. filament current is adjusted to constant strength by a 20-ohm variable resistance R<sub>1</sub> and milliammeter M. The control of filament current is the principal experimental difficulty; it was found desirable to allow the accumulator B<sub>1</sub> to discharge slowly for some hours through a 20-ohm resistance after charging up, to diminish the slight fluctuations in voltage which often occur after charging. A 3-volt "grid bias" battery B<sub>3</sub> maintains a suitable negative potential on plate A, and also on a guard ring GR, of wire tightly coiled round the base of the valve. P is an accurate potentiometer and S a standard cell. The paraffin block E permits A to be connected either with the guard ring or with the standard cell and potentiometer.

The zero is obtained by connecting plate A with the guard ring and



balancing current through the galvanometer by justing R<sub>3</sub>. Readings of the galvanometer are calibrated in terms of potential on the plate by joining the two lower cups on E, and noting the deflections of G for given settings of P, the voltage of the standard cell being subtracted from the reading of P. When taking readings of surface potential, all pools on E are left disconnected. As a rule, the greater part of the

surface potential is balanced out on the potentiometer, amounts less than 100 mv. being found from the deflections of G. This arrangement gives results correct to about 1 millivolt in 4 seconds; it is much more rapid than the Dolezalek electrometer, and is probably more convenient than a Lindemann electrometer.

The solvents used for spreading were chloroform for the trimethyl and triacetyl cellulose, and benzene-alcohol (5:2 by volume) for the benzyl cellulose. N/400 HCl was the underlying solution unless otherwise stated.

The materials were the same as used before; we are indebted to Professor K. Hess, of Berlin, for specimens of crystalline trimethyl and triacetyl cellulose, and to Imperial Chemical Industries, Ltd., for the benzyl cellulose.

<sup>Made by the General Electric Co., Ltd., Wembley.
J. Chem. Soc., 1528, 1930.</sup> 

### Results.

Fig. 2 is for trimethyl cellulose; Fig. 3 for benzyl cellulose (containing 2.66 benzyl groups per hexose group); and Fig. 4 for triacetyl cellulose.

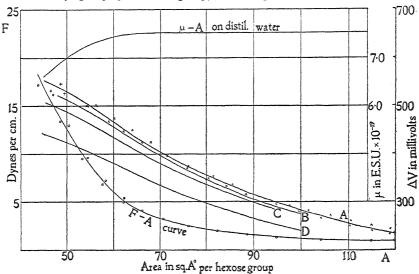


Fig. 2.—Trimethyl cellulose; ΔV-A curves.

A. 0.0025 N HCl. B. Distilled water.

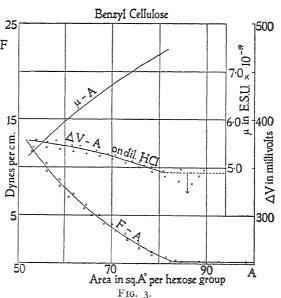
C. 0.010 per cent. picric acid. D. 0.225 per cent. picric acid.

Areas per hexose group are plotted horizontally and surface pressures (F), surface poten-

tials  $(\Delta V)$ , and the quantity  $\mu$ , vertically.  $\mu$  is derived from the surface potential by the Helmholtz equation

$$\Delta V = 4\pi n\mu$$
 . (1)

n is the number of hexose groups per sq. cm. It is related to the vertical component of the dipole moment the hexose groups in the film, but contains also effects due to the rearrangement of water molecules and ions near the surface, caused by the film.



# Trimethyl Cellulose.

Trimethyl cellulose shows a constant value of  $\mu$  above 70 sq. Å. per hexose groups, which is approximately the area at which Adam <sup>1</sup> concluded, from surface pressure measurements alone, that the hexose rings were closely packed, lying flat on the surface. At smaller areas,  $\mu$  decreases, indicating probably that the hexose groups become tilted to the surface so that the vertical component of the dipole diminishes. Above 70 sq. Å., the value of  $\mu$  is constant up to 140 sq. Å., and the surface is homogeneous, the variations of surface potential from place to place not exceeding 5 mv. Above 150 sq. Å., fluctuations in the

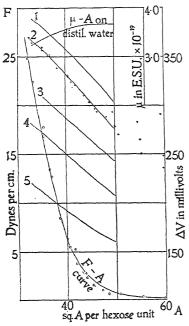


Fig. 4.—Triacetyl cellulose;  $\Delta V$ -A curves.

- I. NHCl.
- 2. Water, 0.0025 and 0.01 N HCl.
- 3. 0.014 per cent. picric acid.
- 4. 0.10 per cent. picric acid.
- 5. 0.50 per cent. picric acid.

surface potential begin to appear, and these gradually increase as the area is increased. At 211 sq. Å., fluctuations of about 22 mv. were found; at 295 sq. A., of about 42 mv. These fluctuations are far less definite than those which usually accompany the break up of a film into two separate well-defined surface phases; the surface pressure curve also exhibits no sudden discontinuities anywhere. It is improbable that the hexose groups, closely packed and stationary, could cover an area much greater than 70 sq. A.; it was suggested in the earlier paper,1 that at low surface pressures the chains may be vibrating so as to exert a surface pressure at areas greater than those at which the chains of hexose groups are closely packed.5 The present surface potential measurements are in full accord with this view; it appears that, from 70 to 140 sq. A., the chains of hexose rings are lying flat in the surface, vibrating so as to cover a space up to about twice that occupied by the chains when stationary. In spite of this vibration, there must still be some lateral adhesion between the chains of hexose groups, since at above 150 sq. A.

gaps begin to appear in the film, producing inhomogeneities in surface potential. This suggests that the flexibility of the chain is sufficient to allow vibrations large enough to cause the chains to cover about twice the area required by a stationary hexose group; as the area is further increased, the lateral adhesion keeps the chains from spreading further, so that gaps appear in the film.

<sup>&</sup>lt;sup>5</sup> Cf. Haller, Kolloid-Z., 49, 74, 1929; 56, 257, 1931. Haller's theory was developed to account for the osmotic and swelling pressure of colloids with long, flexible molecules, in three dimensions; since surface pressure is strictly a two-dimensional osmotic pressure it is obviously also applicable to surface pressure.

## Benzyl Cellulose.

Benzyl cellulose (2.66 benzyl groups) forms a coherent film, tending to 84 sq. Å. per hexose at no compression. At larger areas it exhibits the characteristic behaviour of a surface partially covered by islands of coherent film, fluctuations amounting to hundreds of millivolts being obtained, and occasionally the potential of 345 mv., characteristic of the completely covered surface at 84 sq. Å., is observed up to much larger areas. There is here no apparent tendency of the films to exert a measurable surface pressure, or to cover the surface uniformly, at areas greater than that at which the whole surface is covered by a tightly packed layer of substituted hexose groups lying flat.

On compression of the film below 84 sq. Å., the value of  $\mu$  falls, rather more markedly than with the methyl cellulose below 70 sq. Å. This is presumably due to the same cause, a reorientation of the dipole of the molecule by tilting of the plane of the ring away from the surface.

# Triacetyl Cellulose.

Triacetyl cellulose forms a film homogeneous in surface potential to 6 mv., at areas less than 48 sq. Å. At larger areas fluctuations appear. less definitely than with benzyl cellulose, but far more pronounced than with trimethyl cellulose; e.g., at 54.4 sq. Å. the fluctuations were about 60 mv., at 59.2 sq. Å., about 100 mv. Evidently the tendency to separate into two surface phases, or into one coherent surface phase with gaps between the islands, is present at all areas above 48 sq. A.; and the fact that very large fluctuations do not appear at areas immediately above 48 sq. A. may be due to one of two possible causes. Either the lateral adhesion is not sufficient to cause the chains to stick together into large, well-marked islands of film, so that the islands and interspaces on the surface are not easily distinguished by the exploring air electrode, which explores a fairly large area in any one position. Or, there may be some tendency, as with methyl cellulose, for the chains to cover an area larger than that at which they are closely packed under small compression, by vibration of the chains. This is much less marked, if indeed it exists at all, than with methyl cellulose. On normal HCl, the surface pressure curve of triacetyl cellulose was identical with that on water; but the surface potential curve was about 25 mv. above that on water, remaining parallel to it.

An attempt was made to spread the acetyl cellulose on solutions of methyl violet and malachite green, to see whether the dye had any influence on the nature of the film; unfortunately the surfaces of these solutions became dirty so rapidly that no accurate experiments could be made, except on methyl violet of 0.004 per cent. strength. On this solution the films were indistinguishable from those on water.

On solutions of picric acid, however, the surface potential was markedly lowered with trimethyl and triacetyl cellulose; the amount of lowering increased with increasing strength of the picric acid. The surface pressure was not perceptibly affected by picric acid.

#### Discussion.

(I) The changes in  $\mu$  are interesting, although it does not yet appear possible to interpret the values in a quantitative manner. Equation (I) assumes the films to consist of two parallel sheets of electric charges

(the two ends of the dipoles of the molecules being in two parallel planes) and if we neglect the dielectric constant of the medium between these sheets,  $\mu$  would be the vertical component of the dipole moment of the molecules. In nearly all cases yet studied, the maximum value of  $\mu$  for groups of which the total dipole moment has been measured is about one-fifth or one-tenth of the value of the dipole moment found by other methods. The effective "dielectric constant" of the surroundings of the molecules in the films appears therefore to be of the order five or ten; it is due no doubt to re-orientation of water molecules and re-arrangement of ions. If we suppose that this "dielectric constant" does not change as the film is compressed by a moderate amount, decreases in  $\mu$  indicate a decrease in the vertical component of the dipole moment of the molecule through re-orientation of the end group. This re-orientation is most marked in the case of the benzyl celluloses; and least marked with the acetyl celluloses, where a compression of some 25 dynes per cm. produces only about 7 per cent. decrease in  $\mu$ .

(2) With acetyl cellulose the limiting area of about 48 sq. Å. is somewhat puzzling. All other cellulose derivatives give an area of 60-70 sq. A. This suggests that the triacetyl cellulose is not fully spread. Yet Zocher and Stiebel 6 failed to find collapsed patches visible under the ultramicroscope; Adam 1 found a few local collapsed patches, and we confirm this, though the appearance does not indicate a great amount of unspread material. We have now found that the apparent area of the triacetate film is the same, on diluting the solution four times; the observations of Davey and de Vore 7 indicate that with nitrocellulose, which is very incompletely spread, more spreading is obtained from dilute than from strong solutions. The apparent value of  $\mu$  is only about half that obtained with the fully spread benzyl and methyl ether; it is calculated on the assumption that the apparent area is the true area per molecule in the film, i.e., that there is complete spreading. If the true area per molecule in the film were larger than the apparent (incomplete spreading), then the value of  $\mu$  would also be larger. in conjunction with the fact that it is difficult to pack the model of a hexose ring into less than 60 sq. A. when lying flat, we think it probable that the triacetate film is not fully spread; but there is just a possibility that this conclusion is incorrect, spreading being complete, and the rings somewhat tilted, at 48 sq. A. and low compression.

(3) The effect of picric acid in diminishing the surface potential can be explained as an adsorption of the acid or its anion below the cellulose film, the film exercising an orienting effect on the molecules or ions of picric acid. There does not appear to be a definite stoichiometric chemical combination between the picric acid and the cellulose film; but the Freundlich adsorption isotherm holds good with fair accuracy. If x is the mass of picric acid adsorbed per unit area, m the mass of cellulose derivative in the films per unit area, c the concentration of picric acid in grams per litre, the Freundlich isotherm gives

$$\frac{x}{m} = K_1 c^{\frac{1}{n}}, \qquad (2)$$

n and c being arbitrary constants. If the picric acid is adsorbed underneath the cellulose as a "gaseous" film, which is very probable, since practically all the films yet investigated which have been formed by

<sup>&</sup>lt;sup>6</sup> Z. physikal. Chem., **147A**, 430, 1930. <sup>7</sup> J. Physical Chem., **35**, 2129, 1931.

adsorption from solution are of the gaseous type, the amount by which the surface potential is lowered,  $\delta(\Delta V)$ , will probably be accurately proportional to the amount adsorbed; hence  $x \propto \delta(\Delta V)$ .

If A is the area per molecule,  $m = \frac{1}{A}$ ; equation (2) then becomes

$$A\delta(\Delta V) = Kc^{\frac{1}{n}}$$

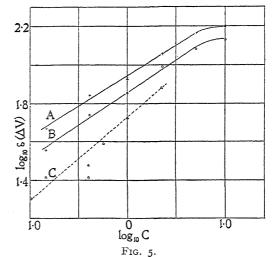
$$\log \delta(\Delta V) = \log K - \log A + \frac{1}{n} \log c. \qquad (3)$$

At any given area, therefore,  $\log \delta(\Delta V)$  plotted against  $\log c$  should

give a straight line. Fig. 5 shows that this is approximately the case, except at the highest concentrations of picric acid. These results may be compared with those obtained by Baur and Kronmann 8 for the potentials produced at the interface between two liquids by adsorption of picrate ions; the relation between the logarithm of the change in potential produced by adsorption of picrate and log c was not so nearly linear, however, in their case as in the present.

or

In the case of triacetyl cellulose, the



A. Triacetyl cellulose at 36 sq. Å.
B. Triacetyl cellulose at 48 sq. Å.
C. Trimethyl cellulose at 60 sq. Å.

values of n and K at different areas are as follows:

Area per Hexose sq. Å.	36.	40.	48.
n	3.11	3.12	2.98
K	3210	3320	3440

The constancy of K and n is as good as could be expected, considering the approximate nature of equation (2) and of the assumptions made.

#### Summary.

Surface potential measurements on films of methyl, benzyl, and acetyl cellulose on aqueous solutions confirm the conclusions drawn from previous measurements of surface pressure, namely, that the hexose rings probably

<sup>&</sup>lt;sup>8</sup> Z. physikal. Chem., **92**, 90, 1916.

lie flat in the surface at low compressions, but are tilted slightly on compressing the films. The vibration of the chains of methyl cellulose, presumed to exist from the large areas occupied under low compressions, appear sufficient to cover areas up to 140 sq. Å. per hexose group with a homogeneous film; at larger areas, there is evidence of small gaps in the film.

Picric acid in solution is adsorbed on to the cellulose films, producing a lowering of surface potential.

The cost of the ultramicroscopic apparatus and of the valve electrometer were defrayed by a grant from the Royal Society Government Grant Committee. One of us (J.B.H.) thanks the Department of Scientific and Industrial Research for a grant.

# THE ATMOSPHERIC CORROSION OF MAGNESIUM.

By L. WHITBY.

Received 21st June, 1933.

In 1830 J. Bussey <sup>1</sup> stated that magnesium becomes covered with the hydroxide after exposure to moist air, but remains unattacked in dry air; Bunsen <sup>2</sup> repeated this statement in 1852. Since that date the writer can find no papers which have dealt with the subject of the atmospheric corrosion of magnesium. This paucity of information is the same for magnesium-base alloys which are vaguely stated by Hiege <sup>3</sup> to become covered with a protective coating of basic magnesium carbonate after exposure to the atmosphere.

The present paper represents an attempt to obtain information on the mechanism of the corrosion of magnesium, and on the nature of the respective corrosion products, after exposure to indoor and outdoor atmospheres.

## Experimental.

Metal used was rolled sheet approximately 0.2 mm. thick, and supplied by the American Magnesium Corporation. Specimens used were cut to  $5 \times 10$  cms. and cleaned first with acetone, then with a steel scratch brush, and finished by lightly rubbing with dried cotton-wool. For exposure to an indoor atmosphere a room in the laboratory building was chosen, in which no chemical operations were performed, and specimens were suspended therein vertically from a punched hole by means of gutta-percha covered copper hooks on a glass rod held by clamps.

For exposure to an outdoor atmosphere specimens were suspended vertically from holes at each corner, by means of gutta-percha covered copper wire, on a wooden stand which was placed, by permission of the Director, National Physical Laboratory, on the flat roof of the High Voltage Building, approximately 80 feet above ground level. The atmosphere there was relatively free from smoke contamination, since prevailing winds came over Bushy Park with no interposed buildings.

<sup>&</sup>lt;sup>1</sup> J. Chim. Méd., **6**, 141, 1830. <sup>2</sup> Annalen, **82**, 137, 1852. <sup>3</sup> Metallwirtschaft, **19**, 361, 1930.

The course of corrosion of both indoor and outdoor specimens was followed by weighing at intervals of first 3 days, then 7 days, and finally 21 days. The weights were obtained to 0·1 mgm. only, the large weight changes rendering further refinement superfluous. After each weighing specimens were changed about before returning to the stands, thereby cancelling any preferential effect of air currents due to the geometry of the stands. The longest period for which specimens were exposed in the indoor atmosphere was 413 days, and for the outdoor atmosphere 217 days.

Metal used contained  $\leq$  99.90 per cent. magnesium, but the specimens, which were duplicated, may not have been entirely identical in composition. Since duplicates agreed excellently, however, it is evident that traces of impurities do not have much effect on the atmospheric corrosion of magnesium. Results of spectroscopic analyses of metal used are given in a previous publication, and specimens were taken indiscriminately from sheets whose composition corresponded to MgC, MgC<sub>1</sub>, and MgC<sub>2</sub> in that communication.

# Discussion.

## Indoor Exposure.

After an exposure of about 14 days the specimens became covered with a thin whitish film which appeared to be thickest at the edges.

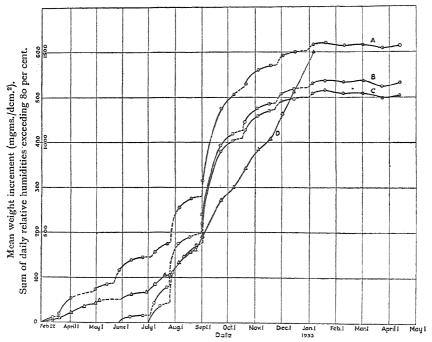


Fig. 1.—Mean weight increment/time curves for magnesium in indoor atmosphere.

Correlation with outside relative humidity.

The film spread and darkened slightly with time but remained smooth and tightly adherent, until at the end of some 400 days the specimens appeared of a light grey colour, and exhibited minute nodules at the

<sup>4</sup> Whitby, Trans. Faraday Soc., 29, 415, 1933.

corners and edges. These nodules were tightly adherent and could not be removed by light rubbing. Sometimes darker coloured lines were visible in the film, but these lines did not consistently appear, and had no untoward effect on the weight increment of specimens so affected. In no case were interference colours visible at any stage of the attack; this suggests that the film does not form a continuous envelope.

Fig. I shows the mean weight increment/time curves of specimens exposed to the indoor atmosphere. Curve A is the main one, and represents over 400 days' exposure, starting at the end of February, 1932. The curve is peculiar, and shows a large number of jumps in the weight increment, sudden increases in the reaction rate occurring at irregularly spaced intervals of time. After each increment in the rate, the curve steadily falls towards the time axis, until there is another sudden jump in the rate. Towards the end of the curve the specimens appear to be actually losing weight, which was not due to loss of any corrosion product.

The reason for the irregular increments in weight was thought to be due either to cracks in the film or to the attainment of a critical concentration at certain periods by some constituent of the atmosphere. The large increases in weight which sometimes occurred seemed to rule out any possibility of the former explanation, since the cracks would have had to occupy a considerable proportion of the surface.

The second explanation was tested by starting further experiments at such intervals of time that when weighed the respective film thicknesses would differ considerably. If the jumps in the reaction rate of all the specimens took place at the same time, irrespective of film thicknesses, then the second explanation would be the more probable.

Comparing A, B and C, it will be seen that all three curves follow each other most faithfully, which rules out the cracking hypothesis completely. It is interesting to note at this stage that the only curves remotely resembling those for magnesium given here were obtained by Vernon 5 for aluminium exposed to an indoor atmosphere. The jumps in Vernon's curves, however, were not nearly so numerous or so marked and were interpreted by the cracking hypothesis.

Influence of Humidity.—The existence of a "critical humidity" in the atmospheric corrosion of iron was suggested by Vernon 6 and was found by him to exist also with copper and nickel in synthetic atmospheres containing sulphur dioxide.<sup>7</sup> Vernon's work, together with that of Hudson 8 on the effect of humidity on the subsequent deliquescence of many atmospheric corrosion products, suggests that humidity may be the controlling factor in the case of magnesium exposed to an indoor atmosphere. Unfortunately, humidity readings taken in the room itself were not available, but in well-ventilated rooms, with no artificial heating, the humidity will closely follow that of the outside air. Outside humidity readings taken in Teddington by means of a sheltered wet and dry bulb instrument were available, and are reproduced here in a modified form by permission of the Director, Paint Research Station. In order to convert daily humidity readings into a form capable of being continuously plotted and suitable for easy correlation with the weight increment/time curves, all readings of less than 80 per cent. were neglected

Trans. Faraday Soc., 23, 153, 1927.
 Ibid., 27, 255, 1931; J. Inst. Metals, 48, 121, 1932.
 Trans. Faraday Soc., 25, 196, 1929. 6 Ibid., 140, 162, 1927.

and the excess of others over 80 per cent. added together, starting with the same time zero as curve A, Fig. 1. The results are shown as curve D, Fig. 1. Those parts of the curve which are parallel or nearly parallel with the time axis represent periods of time during which the humidity was never for long above 80 per cent. All other parts of the curve show periods of high humidity, the slope of the curve indicating the time and amount by which the 80 per cent. was exceeded. It will be seen that during the early parts of the curves an undoubted relation exists between humidity and the weight increments of the specimens: when the humidity curve falls towards the time axis the weight increment remains low, but when humidity rises above 80 per cent. the weight increment rises at a rate which follows the slope of the humidity curve. A slight time lag is noticeable before the weight increment begins to rise after a rise in the outside humidity, but this is to be expected. During the later parts of the curve, however, humidity remains high, but the weight increment shows little change; this is probably due to the fact that the films were then thick enough for atmospheric interdiffusion to be so cut down that they became protective. Moreover, artificial heating began after October.

In order to test still further the critical humidity hypothesis, magnesium specimens were exposed to air, in flasks over sulphuric acid mixtures of

known vapour pressures, and weighed after fixed times. Flasks of 1.5 l. were used containing 110 c.c. of the acid mixtures. Relative humidities at 25° C. of 50, 75, 90 and 100 per cent. were used, and each humidity was duplicated. The flasks were closed by rubber bungs into which thin glass hooks were inserted, and from these the specimens were suspended, folded into V shape, to hang in the body of the flasks. The flasks were kept in an air thermostat at 25° C., and specimens were weighed at intervals up to 77 days. No attempt was made to purify the air in the flasks, and weight increments of the specimens showed that most of the resulting films must have consisted of magnesium hydroxide, since the carbon dioxide content of the air in the flasks was far too low to be considered.

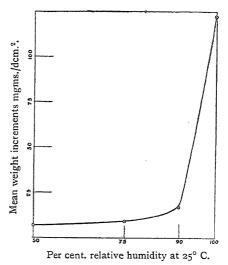
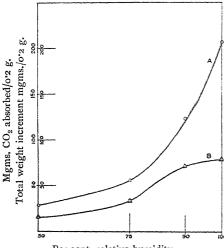


Fig. 2.—Effect of humidity on the action of air on magnesium.

In Fig. 2 are shown the mean weight increments after 77 days plotted against relative humidity. A large rise occurs in the weight increment between 90 and 100 per cent. relative humidity and hence confirms the critical humidity hypothesis advanced above.

In order to explain the reaction between magnesium and moist air we may assume that magnesium hydroxide is formed by a direct reaction between the metal and water vapour in either presence or absence of oxygen. The basic character of magnesium hydroxide coupled with the carbon dioxide content of the atmosphere, suggests that in actual practice

a secondary formation of carbonate may occur. It is known that moist magnesium hydroxide will rapidly absorb carbon dioxide, but so far as the present author is aware no experiments have been performed to test the effect of humidity on this reaction. There is a possibility, therefore, of the existence of a critical humidity for the reaction between magnesium hydroxide and moist air containing carbon dioxide. The existence of such a critical humidity would mean that the sudden increases in the reaction rate for magnesium could be explained not only by increased reaction with moist air to form hydroxide, but also by an increase in the secondary formation of carbonate at certain humidities. To test this point, magnesium hydroxide was dried at 100° C., until of constant weight, and was then exposed to air containing carbon dioxide over sulphuric acid mixtures of known vapour pressures. Quantities of 0·2 g. of the magnesium hydroxide were placed in small glass "buckets" made from shortened specimen tubes 2·3 cms. diameter and suspended from glass hooks inserted in rubber bungs which closed the mouths of 1·5 l. glass



Per cent. relative humidity.

A = total weight increment. $B = \text{weight increment due to } CO_2 \text{ only.}$ 

Fig. 3.—Effect of humidity on reaction between moist carbon-dioxide and magnesium hydroxide at 25° C.

flasks each containing 110 c.c. of the required sulphuric acid mixture. The mixtures used corresponded to 50, 75, 90 and 100 per cent. relative humidity at 25° C. By means of glass stopcocks inserted through the bungs, the flasks were evacuated, 100 c.c. of carbon dioxide were introduced by a burette and the pressure brought to atmospheric by allowing air to enter slowly. The flasks were placed in an air thermostat at 25° C., and allowed to remain for 4 days, after which they were reevacuated, the same quantity of carbon dioxide introduced, refilled with air and allowed to remain in the thermostat for another 10 days. At the end of this period they were removed and the increases in weight of the magnesium hydroxide determined. The carbonate content of each sample was then determined by a

gravimetric method, evolved carbon dioxide being absorbed in a weighed U tube containing Sofnolite. The differences represented combined or absorbed water; results are shown in Fig. 3.

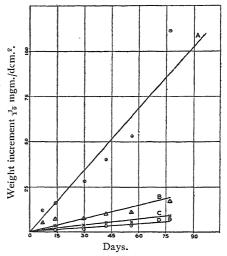
Between 75 and 90 per cent. relative humidity there is a distinct jump in the quantities of both water and carbon dioxide absorbed, and the shape of the weight increment/time curves in Fig. 1 cannot, therefore, be explained solely by reference to the primary attack of the metal; secondary changes in the corrosion product must be taken into account. The argument may be advanced that carbonate is formed by direct action of water vapour and carbon dioxide on the metal, and that this is the primary reaction; it will be shown later, however, that this view is not tenable.

In the light of these results we now have an admirable hypothesis to explain the jumps in the curves A, B and C of Fig. I, since each branch is approximately an inverted form of the curve in Fig. 2 and of curve A, Fig. 3. Actually it might be supposed that if the relative humidity could be kept constant, the weight increment/time curve for magnesium

in an indoor atmosphere would be a straight line, since the corrosion product is probably granular and non-protective like zinc.9 Certainly at high temperatures the oxide film formed on magnesium remains perfectly porous. 10 It is, however, dangerous to assume that films formed at high temperatures have the properties of those formed at ordinary temperatures; even if chemical identity could be assumed, their physical condition would undoubtedly be different. It is fortunate, therefore, that this "straight-line hypothesis" can be checked by direct reference to the figures obtained for the plotting of Fig. 2. For each of the humidities investigated the specimens were weighed not only at the final time of dismantling, but at frequent intervals during the course of the reaction. Results are shown in Fig. 4, and at 50, 75 and 90 per cent. relative humidities good straight lines are obtained. The probable existence at

100 per cent. relative humidity of films of liquid water on the specimens make the errors large in this case, but nevertheless, it seems difficult even here to draw a mean curve representing anything but a straight line.

In Fig. 1 curves A, B and C undoubtedly show a large drop in the reaction rate towards their ends in spite of the fact that the critical humidity must have been exceeded often during this This fact is hardly period. explainable on the "straightline hypothesis," but it should be remembered that the film continually undergoing secondary chemical changes consequent to absorption of carbon dioxide and water and which must result in considerable changes in its primary granular structure. The exist-



A = 100 per cent. relative humidity. B = 90, ,,

C = 75, D =50 ,,

Fig. 4.—Effect of humidity on weight increment/ time curves of magnesium in air.

ence of loosely combined water in the film is well brought out by the actual losses in weight shown near the end of the curves, which, in these cases, are only to be explained by the loss of water owing to temperature and humidity changes in the atmosphere. The probability of the closing of pores in a magnesium hydroxide coating by absorption of carbon dioxide and water is made evident by the specific gravities of brucite (natural magnesium hydroxide) and of nesquehonite (natural trihydrated magnesium carbonate) which are 2.4 and 1.83 respectively, according to Dana.11

A photomicrograph of a portion of the film, taken at the end of 412 days, is reproduced in Fig. 6, and shows the nodules already mentioned.

<sup>9</sup> Vernon, Trans. Faraday Soc., 19, 863, 1924. 10 Pilling and Bedworth, J. Inst. Metals, 29, 577, 1923. <sup>11</sup> A System of Mineralogy, John Wiley, 6th edition.

These nodules appeared under the microscope to be sometimes transparent, and sometimes white, and may be due to small clumps of hydrated magnesium sulphate, sometimes partially dehydrated, since it is known that the septahydrate will effloresce in dry air. The granular nature of the background film is clearly shown.

## Outdoor Exposure.

After exposure to the outdoor atmosphere the specimens became rapidly covered with a smooth light grey film which in time merely darkened and after rain took on a lighter hue.

In Fig. 5 curve A is shown the mean weight/increment time curve for magnesium exposed to the outdoor atmosphere already described. It will be seen that during the course of nearly 220 days there is no indication whatever of a protective film forming; indeed, the weight increment becomes negative after some time. Rainfall is plotted in the same

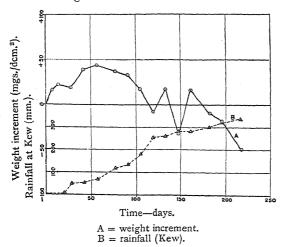


Fig. 5.—Weight increment/time curves for magnesium exposed to outdoor atmosphere and correlation with rainfall (Kew).

figure, curve B, and would be expected, the film only thickens during a dry period and loses weight during rain, owing to the more or less selective removal of soluble constituents. The rainfall figures were obtained at (which is sufficiently near to Teddington to have the same rainfall except for local purely and are showers), published by perof mission the Meteoro-Director, logical Office.

though it should be remembered that the direction of the rain during a shower determines to a great extent the actual amount removed from the films, it will be noticed that during the later stages of the attack, a small amount of rain is able to remove soluble material from the coating to a much larger extent than during the earlier stages. This suggests that the formation of the soluble matter is a secondary phenomena, and is probably connected with the formation of sulphate, since rain near towns contains sulphuric acid. Hence, the actual washing of the film with rain will convert it slowly into sulphate which should, therefore, be present to a much larger extent in the films resulting from outdoor exposure than in the indoor exposure films. The analyses, to be described later, show that this is so.

The action of an outdoor atmosphere on magnesium is probably represented by a primary formation of hydroxide which rapidly absorbs carbon dioxide to form carbonate, and which in turn is slowly decomposed to form sulphate, so that the film is continually forming, becoming



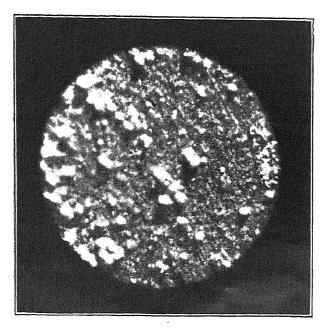


Fig. 6.—Photomicrograph of film produced by 412 days' indoor exposure.  $\times$  70.

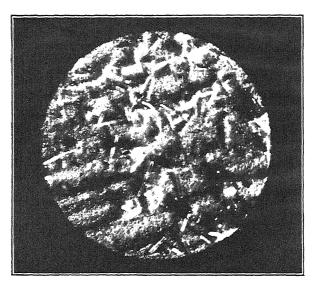


Fig. 7.—Photomicrograph of film produced by 77 days' outdoor exposure.  $\times$  80. [To face page 851.

converted to a soluble form and then being washed away. It is interesting to note that copper exposed to non-marine atmospheres, develops a coating of basic sulphate, which, since it is insoluble, is protective. In the case of magnesium, however, the absence of basic sulphates causes the final film to be soluble, so that as long as there is rain, corrosion proceeds. In several instances during exposure minute, glittering crystals were observed along the edges of the specimens; these crystals were not visible directly after rain. A photomicrograph of them is shown in Fig. 7 and clearly shows their shape; they appear remarkably similar to crystals of septahydrated magnesium sulphate. As in Fig. 6, the granular nature of the background film can be clearly observed.

# Analysis of Corrosion Products.

Owing to the extreme thinness of the coatings, chemical analysis was a matter of some difficulty and scraping the specimens introduced a probability of removing metal. The analyses must, therefore, be considered approximate only.

Indoor Exposure.—The films were so thin that all ideas of scraping off the corrosion product were abandoned and another method was used, based on the good agreement of the weight increments of duplicate specimens. One of a pair of duplicates was cut into small pieces, and the pieces introduced into the flask of a carbon dioxide evolution apparatus for the gravimetric determination of carbonate.13 The large volume of hydrogen that would have been released from the usual evolution acids made it necessary to use an acid which, although decomposing carbonates, would not attack magnesium. It has been shown 14 that a 20 per cent. solution of pure chromic acid is capable of this action, and it was accordingly used. After determining carbonate, sulphate was determined in the acid by addition of barium nitrate and a little hydrochloric acid to the boiling mixture. Although barium chromate is soluble in strong chromic acid, after filtering the barium sulphate through a Gooch crucible the residue was coloured yellow, and repeated washing with water did not remove the colour. washing with a fresh, hot solution of chromic acid, and then water, the residue became white and was ignited. Magnesium was determined indirectly in the weighed duplicate specimen by a selective dissolution of the film with a boiling 20 per cent. solution of pure chromic acid, washing in dry acetone, drying and re-weighing. This gave the total weight of the film, and since the increase in weight of this specimen due to film formation was known, the magnesium content of the film was determined by difference. The magnesium equivalents of the [CO<sub>3</sub>]" and [SO<sub>4</sub>]" contents were then calculated and excess magnesium over this amount was considered to be present as hydroxide. The rest of the film was considered to be water. Oxide was assumed to be absent, since magnesium oxide calcined at low temperatures will rapidly become hydrated in presence of water vapour.15

The results of analyses of films from specimens exposed for 412 and

300 days are given in Table I.

In spite of the differences in the times of exposure, the compositions are seen to be almost identical, and, excluding a coincidence, provide a good check on the accuracy of the analysis. Carbonate and hydroxide are probably present, in part, as a hydrated basic carbonate, and sulphate undoubtedly exists as a hydrated compound. The variation in the com-

Vernon and Whitby, J. Inst. Metals, 42, 181, 1929.
 Ibid., J. Soc. Chem. Ind., 47, 255T, 1928.
 Whitby, J. Soc. Chem. Ind., 50, 83T, 1931.
 Anderson, J.C.S., 87, 257, 1905.

TABLE I.—Composition of Corrosion Products from Magnesium Exposed to an Indoor Atmosphere.

Commercial	Time of Expo	sure (Days).
Composition.	412.	300.
${ m MgCO}_3$	46.5	46.6
${ m MgSO}_{4}$	9.8	9.7
$Mg(OH)_2$	16-3	15.5
$\rm H_2O$	27.4	28.2

position of these loosely combined hydrates with atmospheric temperature and humidity, however, would render any attempts to guess their actual compositions futile.

The presence of sulphate in films produced by an indoor atmosphere is interesting, as it shows that rain is not necessary for its formation; moreover, a mechanism involving a primary formation of magnesium sulphide is untenable, since magnesium will not combine with hydrogen sulphide. The presence of magnesium hydroxide which cannot be formed by hydrolysis in these cases, points to the primary formation of this compound and to the formation of carbonate and sulphate as secondary reactions, as previously suggested.

Outdoor Exposure.—After dismantling the specimens, the film was thick enough to scrape and a steel blade was carefully used; a total quantity of less than 100 mgs. was obtained, however, since care had to be exercised to avoid removing metal.

The corrosion product was heated at 100° C., until constant in weight. Carbonate was then determined gravimetrically, using phosphoric acid as the evolution acid. A separate portion of corrosion product was taken to dryness with hydrochloric acid, redissolved with addition of some nitric acid and insoluble matter determined by filtration through a Gooch crucible, drying at 100° C. The residue, after ignition, was re-weighed, and siliceous and carbonaceous matter were thus determined. In the filtrate, sulphate was determined as barium sulphate, and magnesium as the 8-hydroxyquinoline compound, after removing iron and aluminium with ammonia. In the case of outdoor exposure the sulphate was considered to be present as the septahydrated compound and carbonate as the trihydrate, since this is the result of the action of carbon dioxide on moist magnesium hydroxide. 16 Magnesium hydroxide was determined as for indoor atmospheres, and the results were calculated on the assumption that all water was combined as shown. The initial calculation was, of course, carried out on the assumption that drying the corrosion product at 100° C., had converted the sulphate to the dihydrate, and the carbonate to the monohydrate. No attempt was made to assign the composition to any particular basic carbonate, since the composition probably varies with climatic conditions. Similarly, no attempt was made to represent the composition as a mixture of the corresponding minerals in the same way as for copper 17, since without X-ray confirmation this is a difficult matter. Compounds identical chemically may be either amorphous or may crystallise in different modifications of a system according to the conditions of formation.

TABLE II.—Composition of Corrosion Product from Magnesium Exposed to an Outdoor Atmosphere for 217 Days.

MgCO <sub>3</sub> 3H <sub>2</sub> O								6r·5
$MgSO_47H_2O$								26.7
$Mg(OH)_2$ .	•		•	•	•	•	•	6.4
Carbonaceous		r .			•	•	•	2:5
Siliceous matt		•	•	•	•	•	•	nil.
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}$	3 .	•	•	•	•	•	•	2.9

Cameron and Robinson, J. Physic. Chem., 12, 561, 1908.
 Vernon and Whitby, J. Inst. Metals, 44, 389, 1930.

Actually attempts were made by Mr. J. Thewlis of the National Physical Laboratory to obtain X-ray diffraction figures by the powder method, both from the film itself and from scrapings. The film itself was found to be too thin to give any result, and scrapings resulted in a halo irrespective of the time of exposure, showing that the material was either amorphous or very finely crystalline.

## Summary.

Weight increment/time curves have been obtained for magnesium exposed to both outdoor and indoor atmospheres during over 200 and 400 days' exposure respectively. In indoor atmospheres the rate of attack is controlled by the relative humidity; if humidity could be kept constant it is considered that a linear relationship of weight increment with time would be obtained, the film, however, normally becomes protective owing to secondary reactions which cause the pores to close.

The primary reaction is thought to be formation of magnesium hydroxide; secondary conversion of this to hydrated carbonate then occurs, and for both of these reactions a critical humidity is shown to exist. Sulphate also forms but does not predominate. The film is usually

a mixture of carbonate, hydroxide and sulphate.

In outdoor atmospheres a considerable proportion of sulphate is found in the film, but even here carbonate predominates. The film always loses weight after rain owing to removal of soluble sulphate; during dry periods the film thickens again. No indication of protective film formation has been observed.

The work has been carried out for the Corrosion Research Committee of the Department of Scientific and Industrial Research, and thanks are due to the Chairman, Professor Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, F.R.S., Director of Chemical Research, for permission to publish.

Chemical Research Laboratory, Teddington, Middlesex.

# THE DISSOLUTION OF MAGNESIUM IN AQUEOUS SALT SOLUTIONS. PART II.

By L. WHITBY.

Received 21st June, 1933.

Part I.¹ described a study of the influence of variations in the small amounts of metallic impurities usually present in commercial magnesium on the rates of dissolution in sodium chloride solutions. Large differences were found according to the impurities present, but in dilute hydrochloric acid solution the rates of dissolution were the same. This suggested that the differences in sodium chloride solution were due to changes in the nature or in the rate of formation of the film of hydroxide formed on the metal.

In the present communication the influence of non-metallic impurities has been investigated, and further facts have been discovered relating to

<sup>&</sup>lt;sup>1</sup> Trans. Faraday Soc., 29, 415, 1933.

the influence of variations in the metallic impurities on the rates of dissolution in sodium sulphate and very dilute sodium chloride solutions.

# Experimental.

Experimental technique was the same as that described in Part I.; all

experiments were performed in duplicate.

A sample of magnesium was received by the courtesy of Professor G. Chaudron of the Institut de Chimie, Lille. This sample (MgU) had been prepared by the new technique of Hérenguel and Chaudron,2 which consisted of subliming the metal at 600° C., and a pressure of less than oor mm., and then melting in argon in a closed vessel to which was fitted a syphon leading to a mould in which the metal was to be cast. By raising the pressure of argon, the syphon filled with molten magnesium, which was thus transferred to the mould. The resulting product, unlike magnesium cast in air, was practically free from nitride and oxide. In order to obtain the metal in a form suitable for dissolution experiments, it was rolled at 400° C. by Messrs. British Maxium Ltd., into sheet 0.2 mm. thick. The final passes were made cold, and the metal was then annealed at 400° C., for 10 minutes.

A sample of redistilled magnesium of American origin (MgRA) was kindly presented to the writer by Messrs. British Maxium Ltd., by whom it was melted in a steel crucible with magnesium chloride-magnesium fluoride flux, and cast into plate form a inch thick. It was then rolled at 400° C., to the required thickness.

The above two samples were compared with MgR a pure sample on which experiments have been published in Part I. Table I. gives analyses obtained from spark spectra on a Hilger type El quartz spectrograph, by the Metallurgical Department (N.P.L.). The method used was a comparison of line intensities with a sample, the chemical analysis of which was known. The analysis of MgR now given differs somewhat from that recorded in Part I., since no standard sample was formerly available. Spectra of MgU were taken before and after rolling and were identical, thus showing that no metallic impurities were introduced by the rolling.

The spectra cannot show the presence of nitride or oxide and in the case of the latter no method exists for its quantitative determination in small quantities in magnesium. Nitride was determined by dissolving weighed quantities of the magnesium in dilute hydrochloric acid, and passing the evolved gases through Arnold bulbs containing further dilute acid. The contents of the bulbs together with the liquid used for dissolution were then poured into a distilling flask, excess of caustic soda added, and the resulting ammonia distilled into dilute hydrochloric acid. Ammonia

		 MgR.	MgRA.	MgU.
Cu Ni		0·003-0·01 nil.	o·oo3-o·o1 slight trace.	0·003-0·01 0·003-0·01
Fe		nil.	0.003-0.01	0.003-0.01
Ca Al	•	slight trace.	slight trace.	slight trace.
Mn		nil.	slight trace.	slight trace.
C. Si	:	slight trace. nil.	slight trace.	slight trace.
Na Pb	•	slight trace. slight trace.	slight trace. slight trace.	slight trace. slight trace.
${\rm Mg_3N_2}$	:	o·10	0.08	< 0.02

TABLE I -ANALYSES OF METAL USED

<sup>&</sup>lt;sup>2</sup> Compt. rend., 193, 773, 1931; 195, 1272, 1932.

in the resulting solution was then estimated colorimetrically in the usual manner. The results are recorded in Table I. In addition, a qualitative microscopic examination for oxide and nitride inclusions was made, the final polishing of the metal being carried out by hand rubbing with a slightly alkaline suspension of alumina. Inclusions were noticed in all the samples, but MgU contained less than either MgR or MgRA.

Effect of Non-Metallic Impurities.—Occluded oxide and nitride may possibly act either as cathodes or as nuclei for the commencement of anodic attack. The curves of Figs. 1 and 1a in which the rate of dissolution in o·1 N sodium chloride solution of MgU is compared with those of the other two samples, show that the presence of inclusions cannot be a controlling factor. MgU is relatively free from inclusions, but its rate of dissolution is higher than that of MgR in which o·1 per cent. of nitride was detected.

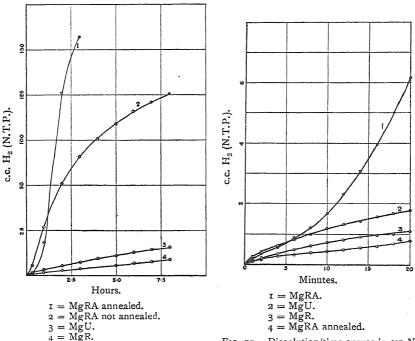


Fig. 1.—Dissolution/time curves in o'1 N sodium chloride solution.

Fig. 1a.—Dissolution/time curves in o'r N sodium chloride solution. Initial action.

The exact function of oxide and nitride inclusions is difficult to settle without samples of magnesium of identical composition except for the inclusions. The preparation of such samples would involve great difficulties, and it remains to determine the effect of inclusions less directly. The figures show that the effect of such inclusions must be less in causing variations in the rate of dissolution than that of metallic impurities.

To determine if it was possible for oxide or nitride inclusions to act either as cathodes or as nuclei for the genesis of anodic action, samples of both MgR and MgRA were carefully polished, washed finally in alcohol and a drop of or I N sodium chloride solution allowed to run over a part of the surface which was being observed through a microscope with a r6 mm. Zeiss objective. In this way many inclusions came within the field of vision and their action during the subsequent attack could be followed; in no case did action appear to start at or adjacent to an inclusion. After

action had commenced, the hydrogen bubbles were apparently evolved from the part undergoing dissolution and never from an inclusion. The reason for the apparent evolution of hydrogen from the anodes was discussed in Part I., where it was suggested that it is discharged at the boundary between anodes and cathodes, bubble formation then occurring on the roughest part of the adjacent surface, i.e., the anodes.

The conclusion may be drawn, therefore, that oxide or nitride inclusions probably play no active part either in initiating or in continuing the attack of magnesium in sodium chloride solution, and that no controlling action is exerted by these inclusions, the variations in rates of dissolution of

different samples being controlled by metallic impurities.

Effect of Metallic Impurities.—The case of MgRA in Figs. 1 and 1a is interesting, since the rate of dissolution accelerated with time from the first few minutes of the attack. The cause is not clear, and only one other case has been recorded, that of MgC<sub>3</sub> in Part I., when it was suggested that the high manganese content was sufficient to cause a progressive redeposition of a manganese compound during dissolution which was able to act cathodically. In the case of MgRA, however, there is an objection to an hypothesis involving redeposition of more noble impurities, since MgU contains even more of these impurities than MgRA, and yet shows the usual decrease of attack with time. Aluminium is, however, exceptionally high in MgU, and can possibly inhibit the redeposition of metallic impurities by enhancing protective film formation. It will be seen that the effect of annealing in vacuo at 400° C., was sufficient to inhibit temporarily the acceleration of attack with time, but that finally the rate became greater than that of the unannealed sample. This phenomena was also observed with MgC3, and seems difficult to explain, unless the redeposition hypothesis is accepted. The initial lowering of the rate may be due to the removal of strain, but the final increase in the rate over the sample not annealed can, as before, be explained by assuming that annealing has increased solid solution of the impurities, so that dissolution of the metal led to increased ease of solution of the impurities with consequent enhanced ease of redeposition. Before annealing the iron may have been present as colonies of some iron-rich phase.

Further light on the mechanism of this accelerated attack was obtained by an analysis of the curves given by MgRA in Figs. I and Ia. The results of single and double logarithmic plots are shown in Fig. 5. It will be seen that from the beginning of the attack the unannealed sample gives a straight line after a double logarithmic plot, but afterwards departs from this linearity. Curve C is a plot of the logarithm of the time against the hydrogen evolution for those latter parts of curve B which depart from the linearity of a log./log. plot. A straight line is obtained which continues until the specimen is almost completely dis-In the case of annealed specimens there is an interim period before the linearity of a log./log. plot obtains, after which the curve resembles that of the unannealed specimen. If the acceleration of attack with time is not due to progressive redeposition of metallic impurities, it may be caused by an absence of protective film formation which enables the primary sporadic distribution of attack to continue unchecked, instead of many of the primary points of attack being removed from further active participation by a film forming over them. If reaction is proportional only to the surface of anodic areas, then in absence of interfering factors such as polarisation and film formation, this surface will be proportional to some power of the time and, therefore, the hydrogen evolved should be proportional to the same power of the time. Consider the ideal case of primary point anodes which develop at a constant rate in three dimensions around the original point, thus becoming hemispheres. The total surface of the hemispheres will be

$$S = 2\pi r^2 N$$

(where N is the number of primary anodes),

and

$$\frac{\mathrm{d}S}{\mathrm{d}r} = 4\pi r N.$$

If the radius increases at the constant rate of dr in time dt, i.e., dr = Kdt,

then

$$\frac{\mathrm{d}S}{\mathrm{d}t} = K4\pi rN = K_1 t \text{ where } K_1 = 4\pi K^2 N.$$

 $\therefore$   $S = \frac{1}{2}K_1t^2$ , the integration constant being zero, *i.e.*, the hydrogen evolution should be proportional to the square of the time. This relation holds not only for the ideal case of hemispherical anodes, but for other three-dimensional anode surfaces, produced by a constant rate of increase in the dimensions of all three axes.

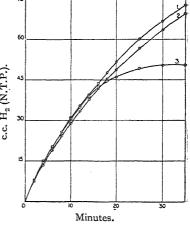
Actually the slope of both curves A and B in Fig. 5 shows that the

exponent is greater than 2, so that there is some accelerating factor other than a simple increase in surface, and this is possibly a cathodic redeposition of a more noble impurity of low overvoltage.

At the point where the curve begins to fall away from a linear log./log. relationship, the metal is broken into small fragments. Near this stage it would be expected that the anodic surface area would decrease with time giving a relationship such as

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{k}{t},$$

where S is total anodic area. If hydrogen evolution is substituted for anodic surface area (assuming proportionality) then integration gives



$$I = MgU$$
.  $2 = MgR$ .  $3 = MgRA$ .  
Fig. 2.—Dissolution/time curves in  $N/5$  hydrochloric acid.

$$(H_2)_t = k \ln t$$
,

and curve C, Fig. 5, shows that this linear relationship between hydrogen evolution and the logarithm of the time does occur in the final period of the attack.

In Fig. 2 are shown dissolution/time curves in 0.2 N hydrochloric acid; duplicate specimens I by 2 cms. were used with a punched hole 3.5 mm. diameter for suspension. The rates of attack in the acid solution were all practically identical, variations shown during the later stages being due to the different thicknesses of the specimens. These curves confirm for the particular samples of metal used a fact recorded in Part I. and found for entirely different samples of magnesium, *i.e.*, that under conditions of no film formation the differences in the rates of attack due to impurities are no longer perceptible.

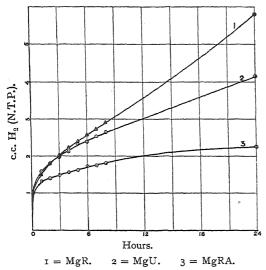


Fig. 3.—Dissolution/time curves o 0002 N sodium chloride solution.

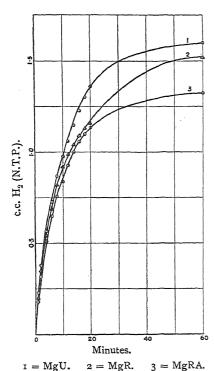


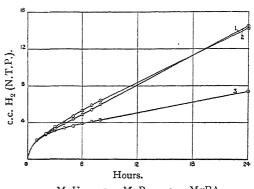
Fig. 3a. — Dissolution/time curves in o ooo N sodium chloride solution. Initial action.

To affect the rates of dissolution in acid solution it would be necessary for impurities to be present to a much larger extent; in small quantities and in presence of a high hydroion concentration gen preferential there is a hydrogen ion discharge at the cathodes. When the hydrogen ion concentration is lowered sufficiently, then the more noble metal ions can discharge at the cathodes sufficiently to cause a progressive increase in the rate attack. In sodium chloride solutions the  $p_H$ soon becomes at least 10.0 owing to saturation with magnesium hydroxide so

that more noble metal ion discharge has a greater tendency to commence.

Effect of Dilution of Sodium Chloride Solution.—In Figs. 3 and 3a are shown dissolution/time curves in 0.002 N sodium chloride solution. During the initial stages of attack the rates of dissolution were of the same order as those measured in O·I N sodium chloride solution (Fig. 1a), but continued for a longer period to be nearly the same for all the samples. ences in the rates commenced after some 10 minutes; the least was shown by MgRA, which in the stronger solution dissolved at a much higher rate than that of the other samples. In the dilute solufilm formation normally and the acceleration of attack with time was inhibited. comparison of Figs. I and 3 shows that MgRA, which gave the greatest rate in the concentration solution, gave the slowest rate in the dilute solution and that MgR which gave the slowest rate in the concentrated solution gave the greatest rate in the dilute solution. This result is curious, and does not seem to be capable of simple explanation. Part I. two explanations were advanced to account for the fact that many of the primary points of attack ceased to show action after a few

minutes, and became covered with a visible One explanation film. was that hydroxyl ion discharge at these primary anodes resulted in a film of magnesium hydroxide capable of altering the potential to a more positive value, so that such film-covered areas became cathodic to the remaining anodes. This caused an increase in the current density at the remaining anodes and impoverishment of hy-



2 = MgR.3 = MgRA.Fig. 4.—Dissolution/time curves in N/10 sodium sulphate solution.

areas, and a tendency, therefore, for the discharge of the next anion in No basic salt or oxychloride forms so preference, the chlorine anion. that dissolution at the remaining anodes continues. Metallic impurities

c.c. H<sub>2</sub> (N.T.P.).

I = MgRA. 2 = MgU. 3 = MgR.Fig. 4a.—Dissolution/time curves in N/10sodium sulphate solution. Initial action.

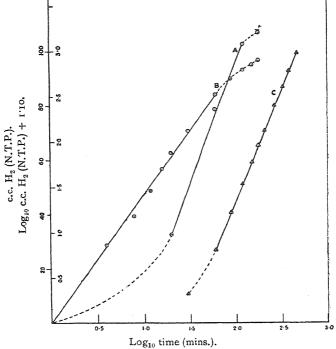
Minutes.

in corroding magnesium will cause changes in the potential of the anodic portions according to the impurities present. Since the metallic impurities must usually be more noble than magnesium the anode potential will probably have a more positive value, the actual value depending on the nature and amount of the impurities and whether they are homogeneously distributed in solid solution or present as intermetallic compounds as segregated impurity-rich In solutions containing phases. large amounts of chlorine ions a smaller number of the original anodes will become film covered before chlorine ion discharge can occur at the remainder, compared with more dilute solutions. Consequently a sample of metal containing noble impurities will tend to dissolve sufficiently in concentrated chloride solutions for surface redeposition of some of the impurities to occur with consequent

progressive acceleration in the rate of attack if these impurities can act cathodically, and have sufficiently low hydrogen overpotentials. In very dilute sodium chloride solutions, however, preferential hydroxyl ion discharge will again occur, but unless the anodic current density reaches a

relatively high value the small quantity of chlorine ion present will not discharge, so that most of the original anodes must disappear before chlorine ion discharge can occur. Consequently, in such dilute solutions noble metallic impurity redeposition cannot occur to any noticeable extent and such impurities only lower the rate compared with that given by a purer sample of metal.

Dissolution in Sodium Sulphate Solution.—In Figs. 4 and 4a are shown dissolution/time curves in O·I N sodium sulphate solution. initial rates, which were almost identical for each sample, were of the same order as those given in 0.1 N and 0.002 N sodium chloride solutions, indicating that the primary mechanism may be the same in each case,



 $\begin{array}{lll} A = MgRA \ annealed. & Log \ T/log \ H_2 \ plot. \\ B = MgRA \ not \ annealed. & Log \ T/log \ H_2 \ plot. \\ C = MgRA \ not \ annealed. & Log \ T/H_2 \ plot \ for \ second \ part \ of \ curve. \end{array}$ 

Fig. 5.—Dissolution/time curves in N/10 sodium chloride solution. Logarithmic plot.

irrespective of the strength of the solution. After about 2 hours differences in the rates appeared and MgRA, behaving as in the 0.002 N sodium chloride solution, gave a rate much below that of the other two samples, which agreed well. The explanation is probably the same as that advanced to account for the differences between the rates of attack in concentrated and dilute sodium chloride solutions, and these results tend to confirm the validity of the hypothesis advanced. The decomposition potentials of alkali metal salts show that in dilute or concentrated sulphate solutions, hydroxyl ion discharge will occur preferentially to that of the sulphate ion; also the reversible discharge potential of the sulphate anion is probably considerably more positive than that of the chlorine anion. Considering the anodic reaction with magnesium in sodium sulphate solutions, therefore, it will be seen that before sulphate anion discharge can take place a considerable local diminution of hydroxyl ion concentration must occur at the anodes, or a large change in the positive direction of the anode potential by a corresponding rise in the anodic current density. The diminution in hydroxyl ion concentration or change in the anode potential before the other anion can discharge will be considerably greater for sulphate than for chloride solutions so that the secondary distribution of attack will consist of less anodes in sodium sulphate than in solutions of equivalent strength of sodium chloride. The lowering of the rate of attack for the less pure sample MgRA in 0·1 N sodium sulphate solution can be explained therefore in the same way as for the 0.002 N sodium chloride solution. It follows that acceleration of attack due to redeposition of metallic impurities can occur only in solutions capable of producing a continuous anodic dissolution, such as chloride solutions sufficiently concentrated. In dilute sodium chloride solution, the mechanism will be similar to that in more concentrated sodium sulphate solutions, considerable hydroxide film formation will occur at the anodes and more noble metallic impurities will lower the rate of attack below that of a purer sample of magnesium. Variations in the rates of attack in moderately concentrated sodium chloride solutions caused by small variations in the metallic impurities present, recorded in Part I., will probably vanish to a great extent when dissolution occurs in very dilute sodium chloride solution or in concentrated or dilute solutions of sodium sulphate. A comparison of Figs. 1a, 3a and 4a shows that in 0·I N and 0·002 N sodium chloride solutions, and in 0.1 N sodium sulphate solution, the initial rates of attack are almost the same, irrespective of the sample of metal used; this confirms the identity of the initial controlling mechanism in each case.

The above comparison of the action of chloride and sulphate solutions provides a reasonable explanation for the fact that the final rate of attack for magnesium is less in sodium sulphate solution than in sodium chloride solution of equivalent strength, no ad hoc assumptions are necessary.

#### Summary.

The effect of inclusions of nitride and oxide normally encountered in magnesium has been examined with reference to their capacity for the initiation or acceleration of corrosion. No evidence could be obtained that these inclusions acted either as cathodes or as nuclei for anodic attack in sodium chloride solution.

The dissolution/time curve of a sample of magnesium which gave accelerated attack with time in o $\cdot$ 1 N sodium chloride solution has been analysed and the conclusion reached that the acceleration was caused by progressive redeposition of more noble impurities.

The influence on rates of dissolution of variations in the metallic impurities is marked in  $0.1\ N$  sodium chloride solution, but small in  $0.002\ N$  sodium chloride or in  $0.1\ N$  sodium sulphate solution. The initial rates of attack were almost identical irrespective of the sample of metal or of the dilution of the solution. The mechanism of attack is discussed.

The work has been carried out for the Corrosion Research Committee of the Department of Scientific and Industrial Research; thanks are due to the Chairman, Professor Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, F.R.S., Director of Chemical Research, for permission to publish, to Dr. G. D. Bengough, for advice and interest, and to Mr. H. R. Sullivan for performing the spectroscopic analyses.

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# ELECTROMETRIC TITRATIONS WITH OXYGEN ELECTRODES.

By J. A. V. Butler and G. Armstrong.

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A number of attempts have been made to use oxygen electrodes in acid-alkali titrations, but it has generally been found that the potentials are liable to fluctuate erratically and the titration curves are not very reliable. We have found that if a platinum electrode is polarised anodically for a short time and then given a very short cathodic polarisation, concordant potentials are observed which vary with the  $p_{\rm H}$  of the solution. In certain cases excellent titration curves may be obtained with electrodes which have been treated in this way.

When a platinum electrode is polarised anodically in a solution in which oxygen is the anodic product, it has been shown 2 that a layer of adsorbed oxygen is formed at potentials considerably less positive than that required for the continuous evolution of oxygen. When the current is stopped the oxygen overvoltage which has been established decays

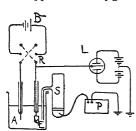


Fig. 1.—Apparatus.

very slowly, and after several hours a nearly constant potential is reached which is a function of the  $p_{\rm H}$  of the solution. This potential has some of the characteristics of reversibility, but it cannot at present be identified with certainty with the reversible oxygen potential. It can be reached much more rapidly by giving the electrode a very short cathodic polarisation, which takes the potential in a short time (a fraction of a second) to the same value, at which it then remains.

The function of the anodic polarisation is thus to establish an adsorbed layer of oxygen on the electrode surface. The subsequent cathodic polarisation destroys the slowly decaying oxygen overvoltage and brings the electrode into a reproducible state in which its potential responds to changes of the  $p_{\rm H}$  of the solution.

The apparatus used in the electrometric titrations is shown in Fig. 1. The bright platinum electrode E and an auxiliary platinum electrode A were connected with a 4-volt battery B through a reversing switch R. The potential difference between the electrode E and a standard half-cell S was measured by means of the potentiometer P and the Lindemann electrometer L. The electrode E was polarised for 10 seconds, and then cathodically polarised for a short time by momentarily closing the reversing switch in the opposite direction. During the titration air or oxygen was sometimes bubbled through the solution, but except as a means of stirring

<sup>2</sup> Butler and Armstrong, Proc. Roy. Soc., 137A, 604, 1932.

<sup>&</sup>lt;sup>1</sup> E.g. J. Furman, J. Amer. Chem. Soc., 44, 2685, 1922; J. Britton, Trans. Far. Soc., 19, 740, 1924. Goard and Rideal have used platinum electrodes which have been treated with oxidising agents such as HNO<sub>3</sub>, KMnO<sub>4</sub> for titrations (J. Chem. Soc.).

this proved to be unnecessary. Mechanical stirring without any passage

of gas was equally effective.

The following table shows the observations made during the titration of 25 c.c. of NaOH (N) with  $H_2SO_4$ . The end point of the titration using phenolphthalein as indicator was at 24.8 c.c.

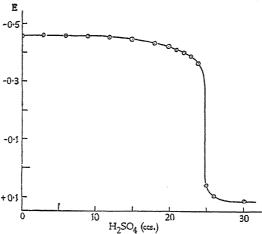
T.	Δ.	R	Γ.	F.	1	-
	٠.	υ.	_	_		

H <sub>2</sub> SO <sub>4</sub> (c.c.).	(1).	(2).	H <sub>2</sub> SO <sub>4</sub> (c.c.).	(1).	(2).
0 3 6 9 12 15	0.476 0.456 0.459 0.458 0.455 0.451 0.443	- 0.457 - 0.461 - 0.459 - 0.458 - 0.454 - 0.448 - 0.432	20 22 23 24 25 26 30	- 0.427 - 0.402 - 0.388 - 0.364 + 0.054 + 0.073 + 0.096	- 0.421 - 0.400 - 0.388 - 0.364 + 0.06 + 0.097 + 0.114

Under column (1) are given the electromotive forces measured immediately after each addition of acid, and under (2) the values after the + polarisations as described above (against the mercurious sulphate electrode). The final values are plotted in Fig. 2. It is not essential to carry out the

+ - polarisation after each addition of acid, but it is better to do so, for after a time the electrode ceases to respond well to the changes of  $p_{\mathbf{H}}$ , if untreated. If the cathodic current is left on too long the potential of the test electrode may rise to the point at which hydrogen is liber-This does not ated. cause any interference for after a few seconds it returns again at open circuit to the characteristic oxygen potential.

When the electromotive force is measured by the ordinary potentio-metric



measured by the or. Fig. 2.—Electrometric titration of NaOH with H2SO4.

arrangement, the values obtained are not so well defined on account of the polarisation of the electrode by the small currents which pass during the determination. Good titration curves have been obtained in this laboratory by students who have had no previous experience of such methods, using a valve potentiometer for observing the electromotive force. Successful titrations have been obtained with nitric and acetic acids. The method fails with hydrochloric acid (owing to interference by chlorine), with easily oxidisable organic acids which may act as oxygen depolarisers, and for some reason phosphoric acid gave rather erratic values.

#### Summary.

Bright platinum electrodes which have been polarised anodically for a short time, followed by a momentary cathodic polarisation, exhibit a reproducible potential which responds well to the  $p_{\rm H}$  of the solution, and may, in the absence of depolarisers, be used for electrometric titrations.

#### THE INFLUENCE OF LYOPHILE COLLOIDS ON PRECIPITATION FROM SOLUTION. GELATIN AND SILVER CHROMATE. PART III.

By Thomas R. Bolam and William J. Donaldson.

Received 6th July, 1933.

The initial process involved in the appearance of a solid phase as the result of interaction between substances in aqueous solution, consists in the production of stable nuclei. Evidence is accumulating 1 to show that the presence of a lyophile colloid may inhibit the formation of such nuclei, so that the system becomes supersaturated with respect to the substance which would normally be precipitated. In the case under consideration, Bolam and MacKenzie i have determined the activity of the silver ion in aqueous mixtures of silver nitrate and potassium chromate containing sufficient gelatin to delay the colour change, from yellow to red, for various time intervals up to 72 hours. It was found that prior to the colour change the activity remained constant at a value much higher than in a pure saturated solution of silver chromate at the same temperature, and that on the appearance of the red colour the activity decreased, the rate of decrease being the greater, the more readily the change took place.2 These observations afforded strong grounds for regarding the development of the red colour as involving the actual formation of solid silver chromate from supersaturated solution, rather than as simply the result of the aggregation of pre-existent solid colloidal particles of that substance.3 The results of the present investigation show conclusively that this view is correct.

The potentiometric data of Bolam and MacKenzie indicated that while the activity of the silver ion in a yellow silver chromate-gelatin mixture may be much greater than in ordinary saturated solution, it is always less than in a pure aqueous solution of silver nitrate at the same concentration as in the gelatin system. This may be due to one or more of the following effects: (I) combination of silver ion with gelatin, (2) formation of un-ionised silver chromate, (3) interionic action between silver ion and chromate or gelatin ion, (4) separation of silver chromate as colloid. It might be thought that the last of these would not be consistent with the formation of a relatively stable supersaturated solution by part of the silver chromate, but the work of Marc, 4 Langdon, 5 and others 6 has shown that gelatin, dyes, and other foreign materials hinder the growth of solid particles immersed in a supersaturated solution

26, 133, 1930.
<sup>2</sup> Similar results were obtained by Desai and Nabar, Trans. Far. Soc., 28,

<sup>&</sup>lt;sup>1</sup> Williams and MacKenzie, J.C.S., 117, 1920, 844. Bolam and MacKenzie, Trans. Far. Soc., 23, 1926, 151 and 162. Bolam, Trans. Far. Soc., 24, 463, 1928;

<sup>449, 1932.

3</sup> Cf. Chatterji and N. R. Dhar, J. Indian Chem. Soc., 5, 175, 1928. Chatterji and J. M. Dhar, ibid., 7, 177, 1930. Hedges, "Liesegang Rings and other Periodic Structures," London, 60-63, 1932.

4 Marc, Z. physikal. Chem., 68, 104, 1910; 73, 685, 1910.

<sup>5</sup> Langdon, Trans. Far. Soc., 19, 285, 1923. 6 See Freundlich, Kapillarchemie. Bd. I., Leipzig, 476, 1930.

of the substance of which the particles are composed. Under these conditions, the supersaturation is not necessarily "released" by the presence of the solid phase. A decision with regard to the abovementioned factors could not be made on the basis of Bolam and MacKenzie's work, since the latter afforded no quantitative information in respect to the chromate ion. In the present research the attempt has been made to account satisfactorily for the whole of the silver and chromate.

It has been found possible to evaluate the degree of supersaturation for a variety of systems and to examine in some detail the influence of concentration and of  $p_{\rm H}$  on the "inhibitive action" of the gelatin. By "inhibitive action" is meant the power of producing supersaturation, as distinct from the other effects which are involved in the non-precipitation.

#### Precipitation Experiments.

The gelatin (C) was supplied by Messrs. Cox Ltd., of Edinburgh, as being a sample of their highest grade of material and comparable with the gelatins (A and B) used in the previous work. It contained 15·2 per cent. moisture, and gave 0·96 per cent. ash, consisting mainly of calcium oxide with a little sulphate (gelatin A gave 1·2, and B, 1·0 per cent. of similar ash). Gelatin C appeared to be more susceptible to bacteriological action than the other samples, and hence only freshly prepared solutions were used. A.R. silver nitrate, potassium chromate and sodium hydroxide, and Kahlbaum acetic acid were employed and all solutions were prepared from specially good distilled water.

Determinations were made of the concentrations of gelatin which just sufficed to delay for 72 hours the appearance of the red colour in mixtures of silver nitrate and potassium chromate at various concentrations and  $p_{\rm H}$  values, the salts being present in exactly equivalent proportions. The procedure adopted was essentially that of Williams and MacKenzie,¹ slight improvements being effected by the use of Pyrex test-tubes, better protection from the action of light, and more exact control of temperature, the tubes being kept in a thermostat maintained at 25  $\pm$  0·1° C. by electrical regulation. In all cases where change occurred, either a light red precipitate appeared in the body of the mixture ("general precipitation") and settled out, provided the system did not gel, or else darker patches of silver chromate formed on the side of the tube. No definite black crystals were observed at the relatively high concentrations investigated, which agrees with previous experience.

The following indicates the method of adjusting the  $p_{\rm H}$  of the system. Into each of a series of uniform flat-bottomed cylindrical tubes were placed 10 c.c. of a 1 per cent. solution of gelatin C and two drops of indicator. Increasing known amounts of o·I N acetic acid or sodium hydroxide were added to successive tubes and colour comparison made with standard buffer solutions lying o·I of a  $p_{\rm H}$  on opposite sides of the desired value. In this manner the proportion of acid or alkali to be added to a given amount of gelatin was estimated with sufficient accuracy, as was shown by checking the  $p_{\rm H}$  of the solution actually used for the precipitation experiments. Methyl red was used except for  $p_{\rm H}=4\cdot3$ , in which case B.D.H. "Universal" indicator was found to be more satisfactory. The sodium acetate-acetic acid mixtures of Walpole ' were taken as standards. A I per cent. solution of gelatin C was found to give a  $p_{\rm H}$  value of 5·3 (cf. 5·0 for A, and 5·7 for B).

The final results are collected in Table IV. and plotted in Fig. 1. In the second column of the table is given the total concentration of silver chromate (which, in the units chosen, is equal to the concentration of potassium

<sup>&</sup>lt;sup>7</sup> See Coles, "Practical Physiological Chemistry," Cambridge, 28, 1920.

chromate, and half that of the silver nitrate) in the system. The third column contains the concentration, in grams of dry material per 100 c.c., of gelatin necessary to prevent colour change within 72 hours. We are indebted to Miss J. G. Ogilvie, B.Sc., for the data at  $p_{\rm H}=5.3$ .

#### E.M.F. Measurements.

The activity of the silver ion in the various systems was obtained by measurement of the e.m.f. of a concentration cell of the type:—

Ag, o.i 
$$M$$
. AgNO<sub>3</sub>, io  $M$ . NH<sub>4</sub>NO<sub>3</sub>, X, Ag.,

where X denotes the system under investigation. Fine pure silver gauze (supplied by Messrs. Johnson, Matthey & Co., London) was used as electrode material. A strip of the gauze was fused to a stout copper wire, held in position in a glass tube by a firm packing of cotton-wool. The upper part of the gauze was coated with paraffin wax and the level of the cell solution adjusted to ensure that the unwaxed portion was completely

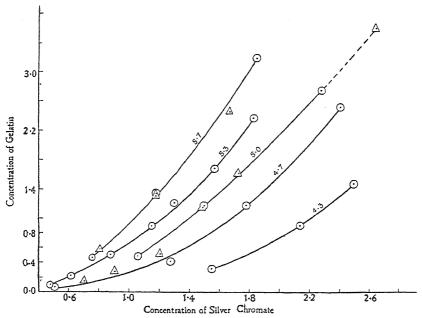


Fig. 1.— $\odot$  = Gelatin C.  $\triangle$  = Gelatins A and B.  $p_H$  values shown.

immersed. Before use, the silver was carefully annealed by heating to dull redness and quenching in cold water. Entirely new electrodes were prepared for each experiment. By adopting the above precautions it was found possible to obtain results which compared very favourably with those given by silver-plated electrodes, whether platinum or silver, and the massive metal electrodes were found to be much more convenient for the investigation of the gelatin systems. All measurements were made at  $25 \pm 0.1^{\circ}$  C., by the ordinary method. The standard cell was checked at intervals against a second cell, calibrated by the N.P.L. In all cases the e.m.f. is expressed in millivolts.

#### Aqueous Systems.

In order to interpret the data obtained for the gelatin systems, it was necessary to investigate the behaviour of the electrodes in some simple aqueous systems.

(a) Solutions of Silver Nitrate.—Table I. gives the e.m.f. values for cells in which X consisted of a pure aqueous solution of silver nitrate. The concentration of this solution is shown in the first column. Readings were made at intervals of half an hour and one hour after placing the cell in the thermostat, and it was found that the difference between the two readings was seldom greater than o-4 millivolt, and usually less. The "experimental" e.m.f. value given in the table is the mean of the half-hour readings. It differs from the individual values by less than o-4 volts in most cases, and in no instance by more than 1-0 volt. The "calculated" value is derived from the usual formula by means of the silver ion activity coefficients suggested by Lewis and Randall. It will be seen that there is fair agreement between the two sets of values, but that the experimental are consistently lower than the calculated. The graph obtained by plotting the experimental e.m.f. against the log. of the calculated activity proved to be a straight line.

TABLE I.—E.M.F. Values for Aqueous Solutions of Silver Nitrate.

Concn. Silver Nitrate.	Number of	E.m.f.			
(Millimols Per Litre.)	Determinations.	Experimental.	Calculated.		
1.00 1.25 1.50 2.00 3.33 4.00	4 2 4 2 2 3 6	111.0 105.2 101.0 92.4 80.6 73.2 53.9	112·3 106·6 102·0 94·7 82·0 77·5 55·1		

(b) Solutions of Potassium Chromate Saturated with Silver Chromate. —In Table III. are given the e.m.f. values for cells in which X consisted of a solution of potassium chromate saturated with silver chromate at  $25 \cdot 0^{\circ}$  C. Silver chromate was prepared by the interaction of solutions of silver nitrate and potassium chromate. The precipitate was thoroughly washed with distilled water and dried in an air oven. A quantity of the solid was placed with the potassium chromate solution in a resistance glass bottle and the mixture well shaken for five hours in the thermostat. The data in Table II. show that the period of shaking was sufficiently long to

TABLE II.—Influence of Period of Shaking on Value of E.M.F.

D	E.m.f.						
Period of Shaking.	₫ hr.	ı hr.	22 hrs.	Mean.*			
4 hrs.	147·3 147·3 148·2	147*3 147*5 147*5	148·1 148·9 146·1	147.6			
18 hrs.	148·7 148·4 148·9	147·3 147·5 147·3	19 hrs. 148·1 148·9 148·1	148.7			

<sup>\*</sup> Mean of ½ hr. readings.

<sup>8</sup> Lewis and Randal, "Thermodynamics," New York, 382, 1923.

ensure saturation. In this particular case potassium chromate was not present and in order to render the null-point sufficiently definite, the system was made  $o \cdot o i$  M. with respect to potassium nitrate. This procedure was adopted whenever the concentration of potassium chromate was low, the effect of the potassium nitrate upon the activity of the silver ion being negligible (cf. Bolam and MacKenzie 1).

The amount of dissolved silver chromate and hence the final composition of the system was obtained in the following manner. It was assumed that the silver chromate was completely ionised, and that the concentration of the silver ion was equal to its activity as calculated from the e.m.f. by taking the activity coefficient in or M, silver nitrate as equal to or 77 (Lewis and Randall,\*). The molar concentration of silver chromate was therefore numerically equal to half the value of the silver ion activity, and the total molar concentration of chromate to the sum of the molar concentrations of potassium chromate and silver chromate.

The  $p_{\rm H}$  of the distilled water was  $6 \cdot {\rm o} - 6 \cdot {\rm f}$  and the acidity was increased by the addition of acetic acid. In order to cover the entire range of e.m.f. values obtained in the gelatin mixtures, measurements were made on the system obtained by saturating 0.0004~M. silver nitrate, at  $p_{\rm H} = 4.3$ , with silver chromate. The e.m.f. for this solution (124.0 m.v.) gives 0.614 millimol per litre as the total concentration of silver present. Of this, 0.4 m. mol. is due to silver nitrate. Hence 0.214 m. mol. is present as silver chromate, and the concentration of chromate is therefore 0.214/2, 0.107 = m. mol. per litre.

In contrast with the experience of Abegg and Cox, and in confirmation

TABLE III.—E.M.F. Values for Solutions of Potassium Chromate Saturated with Silver Chromate.

₽ <sub>H</sub> .	Concn. K <sub>2</sub> CrO <sub>4</sub> (m. mols./litre).	E.m.f.	Total Chromate (m. mols./litre).
6.0–6.5	0.00	148-1	0.120
,,	0.50	171.8	0.249
,,	1.00	179.0	1.040
,,	1.69	185.5	1.660
5.3	0.00	146.2	0.130
5.0	0.00	145.9	0.131
4.7	0.00	142.0	0.153
,,	0.10	149.5	0.214
,,	0.20	156.2	0.289
,,	0.50	171.5	0.549
"	1.66	186-1	1.690
4.3	(0.40)*	124.0	0.107
,,	0.00	135.8	0.195
,,	0.10	145.8	0.232
,,	0.20	152.3	0.302
,,	0.50	167.5	0.557
,,	1.66		1.690
	[		1

<sup>\*</sup> Silver nitrate.

of that of Bolam and MacKenzie,¹ the potentials observed in the present work were found to be steady and reproducible, the limits of variation being about the same as in the case of the silver nitrate solutions. Three determinations were made on each system. The e.m.f. obtained for a saturated solution of silver chromate in distilled water is in good agreement with that observed by Bolam and MacKenzie,¹ the values being 148·1 and 147·4 m.v. respectively. Smooth curves were obtained on plotting e.m.f. against total chromate.

<sup>9</sup> Abegg and Cox, Z. physikal. Chem., 46, 6, 1903.

#### Gelatin Systems.

(c) Mixtures of Gelatin, Silver Nitrate, and Potassium Chromate ("Supersaturated" Systems).—The fourth column (c) of Table IV. gives the e.m.f. values for cells in which X consisted of a mixture of equivalent amounts of silver nitrate and potassium chromate with just sufficient gelatin to prevent visible change in 72 hours. Each figure represents the mean value of the half-hour readings for at least three determinations.\* The whole of the results are given, except for a few experiments in which the e.m.f. changed by more than 1.0 m.v. between the half-hour and hour readings. More often than not the change was considerably less than 1.0 m.v. No complete explanation can be given for the cases of exceptionally rapid change, but it was usually found to occur with electrodes which gave values greater than 54.4 m.v. and less than 53.2 m.v. when tested in the cell o·I M. AgNO<sub>3</sub> - o·oI M. AgNO<sub>3</sub> prior to measurement in the gelatin system. All the electrodes used for the experiments with gelatin of  $p_{\rm H}=5.3$  were so tested and found to conform to the above limits. The agreement between duplicates was not so good as in the case of the simple aqueous solutions. However, the mean values given in Table IV. are probably correct to within a millivolt. The e.m.f. values at  $p_{\rm H}=5.7$  do not differ greatly from those obtained by Bolam and MacKenzie <sup>1</sup> for three very similar systems containing gelatin B ( $p_{\rm H}=5.75$ ).

(d) Mixtures of Gelatin and Silver Nitrate.—In the fifth column (d) of Table IV. are given the e.m.f. values for cells in which X consisted of a mixture of gelatin ( $p_H = 5.3$ ) and silver nitrate alone, the concentrations being the same as in the mixtures containing both silver nitrate and potassium chromate. The degree of constancy and of reproducibility of e.m.f. was found to be the same in the absence as in the presence of the

latter salt.

(e) Mixtures of Gelatin and Potassium Chromate, Saturated with Silver Chromate ("Saturated" Systems) —In the sixth column (e) of Table IV. are given the e.m.f. values for cells in which X consisted of a mixture of gelatin and potassium chromate, saturated with silver chromate at 25.0° C. The concentration of potassium chromate was such that the total chromate concentration had the value given in the second column of the table. Saturation with silver chromate was attained by the procedure described under b. The data in Table V. show that shaking for a period of five hours was again sufficient. System A consisted of 0.85 per cent. gelatin at  $p_{\rm H}=5.3$ , and system B of 1.69 per cent. gelatin ( $p_{\rm H}=5.3$ ) + 1.19 m. mols per litre of potassium chromate. In the case of B the mixture soon gelled and the large amount of solid silver chromate which had been added remained dispersed throughout the mass. While the figures for the last two experiments are appreciably lower than the others, the difference does not exceed the possible error.

The following indicates the method of obtaining the e.m.f. values for "saturated" systems containing the same amounts of gelatin and total chromate as the "supersaturated" systems. Since there was combination between the gelatin and a portion of the silver ion, † the amount of silver chromate which dissolved could not be obtained directly from the e.m.f. as in the case of the aqueous systems (see under b). Measurement was therefore made of the e.m.f. in systems containing the same amount of gelatin and suitable amounts of silver nitrate, ‡ and that concentration, in m. mols per litre, of the salt which gave the same e.m.f. as the "saturated" system taken as equal to twice the concentration, in the same units, of silver chromate in the latter. An actual example may be quoted to show the

complete procedure.

\* This applies to all the figures in Table IV. † See "Discussion." † In the initial experiments the mixtures also contained potassium chromate at the same concentration as in the "saturated" system. It was found, however, that the e.m.f. was the same in the absence as in the presence of this salt.

TABLE IV.—E.M.F. VALUES FOR GELATIN SYSTEMS.

A	Concn. Silver	Concn. Gelatin			
$p_{ m H}$ .	Chromate (m. mols./litre).	(per cent.).	c.	đ.	e.
5.7 ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	0·76 1·18 1·85 0·48 0·62 0·88 1·15 1·30 1·39 1·45 1·57 1·68 1·83 1·06 1·50 2·28	0.46 1.34 3.20 0.10 0.22 0.51 0.90 1.22 (1.37)* (1.48) 1.69 (1.97) 2.38 0.49 1.18 2.77	111.6 108.2 109.9 116.6 113.2 108.7 104.7 104.3 104.1 103.9 104.2 103.9 99.9 96.1	II7·3  II0·1  I03·4  I03·9  I04·1  I04·0	167·6 169·4 166·3 165·1 166·3 165·0 163·3 155·6
4·8-4·9 " 4·7 " " 4·3 "	1·11 1·58 0·51 1·28 1·78 2·41 1·55 2·14 2·50	0.47 1.16 0.07 0.42 1.19 2.54 0.32 0.91 1.49	99.7 94.1 112.9 96.6 92.3 86.2 88.1 81.1		161·9 151·1 165·3 152·6 142·8 — 142·2 130·4 130·5

TABLE V.—Influence of Period of Shaking on Value of E.M.F.

		E.m.f.						
System.	Period of Shaking.	∄ hr.	ı hr.	22 brs.	Mean.†			
$\overline{A}$	5 hrs.	143.0 144.8 144.0	145·2 144·5 145·2	(140·3) 143·0 144·0	143.9			
	18 hrs.	144.0 144.7 144.7	144·9 144·7 144·7		144.2			
				20 hrs.				
В	5 hrs.	165·8 165·8 165·8	165·4 165·8 165·2	165·0 165·0 165·2	165.8			
	II hrs.	165·4 166·3	164·5 167·2		165.8			
				2 hrs.	,			
	5 hrs. + 3 days standing	163.5	164.2	164.4	163.7			
٥	11 hrs. + 2 days standing	163.9	163.0					

<sup>\*</sup> Values in brackets obtained by interpolation on graph in Fig. r.  $\dagger$  Mean of half-hour readings.

Composition of "supersaturated" system:-

Gelatin ( $p_{\rm H}=4\cdot3$ ) = 0.91 per cent. Silver nitrate = 4.27 millimols per litre. Potassium chromate = 2.14 ,, ,,

E.m.f. values in "saturated systems" containing 0.91 per cent. gelatin  $(p_{\rm H}=4.3)$ —

E.m.f. values in mixtures of o-91 per cent. gelatin ( $p_{\rm H}=4\cdot3$ ) and silver nitrate—

The values of y corresponding to the e.m.f. values for the "saturated" systems were obtained, by interpolation, from the straight-line graph produced by plotting the experimental y values (see above) against the corresponding e.m.f.'s. It is evident that the total concentration of chromate in a "saturated" system is given by x + y/2. The values of this quantity for the three systems examined are shown in the accompanying table.

	"Saturated" System.		x.	E.m.f.	y (Derived).	Total Chromate.		
I. II. III.	:	•	•	•	1·61 1·89 2·47	124·6 131·7 137·7	0·80 0·62 0·48	2·01 2·20 2·71

In view of the possible experimental error (about 2 m.v.) we may say that the e.m.f. changes by 0.22 m.v. for a change of 0.01 in the total chromate concentration. Hence the value for the e.m.f. in the case of the "saturated" system with the same total chromate as the given "supersaturated" system, viz., 2.14 m. mols per litre, is  $131.7 - 100 (2.20 - 2.14) \times 0.22 = 130.4$  m.v.

#### Discussion.

Reproducibility of Data.—It is of primary importance to enquire how far the data obtained in the present investigation agree with the results of the earlier work. The points for the "supersaturated" systems obtained with gelatins A and B are therefore shown in Fig. I, along with the curves for gelatin C. Gelatin A gave a  $p_{\rm H}$  value of 5.0, and it will be seen that Williams and MacKenzie's points for this gelatin, without addition of acid or alkali, lie close to the curve for gelatin C at the same  $p_{\rm H}$ . Again, untreated gelatin B gave a  $p_{\rm H}$  value of 5.75 and the points for this gelatin, due to Bolam and MacKenzie,\* are near those for gelatin C at  $p_{\rm H}=5.7$ , except at the highest concentration, where the agreement is only fair. Bolam and MacKenzie's systems for gelatin A at  $p_{\rm H}=4.7$ , however, all lie somewhat above the 4.7 curve for gelatin C. In this case, gelatin A was treated with acetic acid and then washed with water for 3 to 5 days, in order to remove salt impurities. Although the washing was carried out at a relatively low temperature (that of tap

<sup>\*</sup> Loc. cit.¹ It should be pointed out that graph III. in Fig. 1 of this paper is in error owing to incorrect plotting of the point for the highest concentration of gelatin.

water) it is probable that a certain amount of hydrolysis of the gelatin took place and, as has been shown by several workers, 10 this has the effect of increasing the concentration of gelatin necessary to delay the precipitation for a given time interval. It therefore appears likely that if gelatin A had been brought to 4.7 by simply adding acetic acid, the agreement with gelatin C would have been close.

From the above, we may conclude that at the same temperature and pH, and under conditions which exclude hydrolysis, gelatins A, B, and C have practically the same power of inhibiting precipitation. It follows that (I) the method of manufacture of these gelatins gives a product which is satisfactorily reproducible in respect to the inhibitive action. and (2) the behaviour of gelatin C may be taken as typical of that of a

high grade material.

**Proof of Supersaturation.**—It would appear from the work of Cumming 11 that the liquid-liquid junction potentials are of negligible proportions in silver nitrate concentration cells with 10 M ammonium nitrate as connecting liquid, and there seem to be no adequate grounds for supposing that the presence of gelatin or potassium chromate, in the electrode solutions of such cells, gives rise to any large diffusion or membrane potential.\* In calculating the activity of the silver ion  $(a_{Ag}+)$  in the various systems investigated, it has therefore been assumed (I) that any liquid-liquid or liquid-gel boundary potentials may be ignored without causing serious error, and (2) that the activity coefficients given by Lewis and Randall 8 are sufficiently exact for the present purpose.

In the fourth column of Table VI. are given the values of  $a_{Ag}$ + in the systems containing silver nitrate and potassium chromate, in equivalent proportions, along with just sufficient gelatin to delay precipitation for 72 hours ("supersaturated" systems). These values have been derived from the potentiometric data (given under c in Table IV.) by interpolation on the straight-line graph drawn from the data for the aqueous silver nitrate cells (see Section a, page 867). In the sixth column (e) of Table VI. are shown the values of  $a_{Ag}$  in the corresponding "saturated" systems, calculated from the appropriate e.m.f. values (e, Table IV.) on the assumption that the activity coefficient of the silver ion is unity at the very low concentrations involved and taking the activity coefficient in  $O \cdot I$  M. silver nitrate as 0.77 (see page 868). Comparison of the two sets of values for  $a_{Ag}$ + reveals that the activity in a system of the first type is always very much greater, actually six to eleven-fold (see last column of Table VI.), than in the corresponding "saturated" system. This proves directly and conclusively that the systems under investigation are strongly supersaturated with respect to silver chromate. The experiments thus show quite definitely that the high activity of the silver ion in these systems is not simply the result of an increase in the solubility of the silver chromate due to the acid in the gelatin, as postulated by Chatterji and Dhar.3

Combination between Gelatin and Silver Ion.—In the third column of Table VII. are given the values for  $a_{Ag}$  in mixtures of gelatin ( $p_{H}=5.3$ ) and silver nitrate, derived from the e.m.f. values recorded under d in Table IV., by interpolation on the graph employed in the case of the

<sup>10</sup> Bolam and Desai, Trans. Far. Soc., 24, 50, 1928. Nabar and Desai, loc.

<sup>11</sup> Cumming, Trans. Far. Soc., 2, 213, 1906.

<sup>\*</sup> See Bolam, loc. cit. Also footnote on page 869 and text on page 871 of present paper.

TABLE VI.—Values of Activity of Silver Ion in Gelatin Systems.

$p_{ m H}.$	Concn. Silver			tivity of Silve (×10³).	er Ion.	Ratio,
<u>-</u>	(m. mols./litre.)	(ref cent.)	с.	d.	c.	е
5.7  5.3    5.0  4.8–4.9	0.76 1.18 1.85 0.48 0.62 0.88 1.15 1.30 1.39 1.45 1.57 1.68 1.83 1.06 1.50 2.28 1.11	0.46 1.34 3.20 0.10 0.22 0.51 0.90 1.22 (1.37)* (1.48) 1.69 (1.97) 2.38 0.49 1.18 2.77 0.47 1.16	0·96 1·09 1·02 0·79 0·90 1·06 1·24 1·25 1·26 1·27 1·26 1·27 1·47 1·69 1·87 1·49		0·112 0·105 — 0·118 — 0·124 — 0·124 — 0·133 0·180 — 0·141	8·6 10·4 — 6·7 — 8·6 — 10·6 — 10·2 — 11·1 9·4 — 10·6 8·5
4·7 ,, ,, 4·3	0·51 1·28 1·78 2·41 1·55 2·14 2·50	0·07 0·42 1·19 2·54 0·32 0·91 1·49	0.91 1.66 1.95 2.44 2.27 2.95 3.68		0·123 0·202 0·295 — 0·302 0·475 0·477	7.4 8.2 6.6 — 7.5 6.2 7.7

<sup>\*</sup> Values in brackets obtained by interpolation on graph in Fig. 1.

The decrease in activity could be attributed to interionic action, or to combination between the gelatin and the silver ion, or to the operation

TABLE VII.—INFLUENCE OF GELATIN ON ACTIVITY OF SILVER ION.

Concn. of AgNO <sub>3</sub> , (Millimols Per Litre.)	Concn. of Gelatin.	Activity of Silver Ion (×10 <sup>3</sup> ).			
	(Per Cent.).	Gelatin Present.	Gelatin Absent.		
0·96 1·75 2·60 2·78 3·13 3·65	0·10 0·51 1·22 1·37 1·69 2·38	0·78 I·0I I·3I I·27 I·26 I·27	0.94 1.69 2.48 2.65 2.97 3.44		

<sup>&</sup>quot;supersaturated" systems. The last column of Table VII. contains the activities for the corresponding pure aqueous solutions of silver nitrate. It will be seen that the activity of the silver ion is depressed by the gelatin, in some cases to a very marked extent. Similar results have been reported by Audubert, 12 Northrup and Kunitz, 13 and Kruyt and Boelman.14

Andubert, Comptes Rendus, 12, 838, 1923.
 Northrop and Kunitz, J. Gen. Physiol., 9, 351, 1925-26.
 Kruyt and Boelman, Koll. Beih., 35, 165, 1932.

of both these factors. In all probability gelatin gives rise to polyvalent ions, and it might be supposed that although the concentration of the protein is small, the ionic strength is relatively large. Simms,  $^{15}$  however, has pointed out that probably the charged groups in the dissolved gelatin molecule are so far apart that the effective valence in acid solution is only 1.8. We may therefore reasonably regard the decrease in  $a_{\rm Ag}^+$  produced by the addition of gelatin as due principally to actual combination.

Combination between Gelatin and Chromate Ion.—It is evident that the e.m.f. in the case of a "saturated" system depends upon the concentration of *free* chromate in the mixture, and so may be employed to ascertain to what extent combination takes place between gelatin and chromate ion. The relation between e.m.f. and chromate ion concentration was obtained by direct plotting of the data given in the last two columns of Table III., and the free chromate in the "saturated" systems estimated by interpolation, using the e.m.f. values under e in Table IV. From Table VIII. it will be seen that in all the systems examined there was combination between gelatin and chromate ion, and that in many instances only a small fraction of the latter remained free.

TABLE	VIII.—CONCENTRATIONS	OF	FREE	CHROMATE	IN	"SATURATED"	,
	S	YST	EMS.				

$p_{ m H}$ .	Concn. of Gelatin. (Per Cent).	Total Concn. of Chromate. (Millimols Per Litre.)	Concn. of Free Chromate. (Millimols Per Litre.)
5.7 5.3  5.0 4.8–4.9 4.7  4.3	0.46 1.34 0.10 0.51 1.22 1.69 0.49 1.18 0.47 1.16 0.07 0.42 1.19	0.76 1.18 0.48 0.88 1.30 1.57 1.06 1.50 1.11 1.58 0.51 1.28 1.78	0.45 0.50 0.43 0.41 0.43 0.41 0.39 0.26 0.36 0.22 0.45 0.25
"	0·91 1·49	2·14 2·50	0·14 0·14

Absence of Colloidal Silver Chromate.—Bolam and MacKenzie <sup>1</sup> found that in the three supersaturated systems examined by them, about one-third only of the silver was present in the form of simple ions.\* Apropos of this result, Chatterji and Dhar <sup>3</sup> remark "We are of the opinion that the two-thirds of silver, which does not exist in the ionic condition, remain in the colloidal state. Hence the measurements of Bolam and MacKenzie are in support of our views that the sparingly soluble substances formed in the presence of gelatin exist as a colloid." As pointed out at the commencement of this paper, it is possible that, in the presence of gelatin, supersaturation may occur, although a portion

<sup>15</sup> Simms, J. Gen. Physiol., 11, 613, 1927-28.

<sup>\*</sup> Confirmed in the course of the present investigation. See page 868.

of the silver chromate has separated in the solid form. The results of the present work, however, do not support the view that the solid phase

is present under the given conditions.

In the first place, as will be seen from Table IV. (c and d), the e.m.f. given by a "supersaturated" system is identical with that given by a mixture of gelatin and silver nitrate at the same concentrations. This means either (I) that the presence of potassium chromate is without influence on the value of  $a_{Ag}$ + and also produces no measurable change at the liquid-liquid junction, or (2) that it alters the value of  $a_{Ag}$  but at the same time gives rise to a junction potential difference of such magnitude and sign that the net effect on the e.m.f. of the cell is negligible. Since the second alternative seems very improbable, it follows that when silver nitrate and potassium chromate, in equivalent concentrations, are brought together in the presence of gelatin of such concentration that no visible change takes place in 72 hours, the activity of the silver ion has the same value as in the absence of the chromate.\* It is difficult to see how this state of affairs can be reconciled with the formation of colloidal silver chromate, for this would entail disappearance of silver from the solution, and the activity of the silver ion would necessarily

In the second place Chatterji and Dhar <sup>3</sup> entirely overlook the possibility of combination between the gelatin and the interacting ions. Actually, as is shown by the equality in e.m.f. in the presence and absence of potassium chromate, such combination accounts exactly for that part of the silver which is not present as simple ion. Moreover, as the result of the experiments on "saturated" systems, we now know that there exists a very strong tendency to combination between gelatin and chromate ion.

The available evidence, then, favours the view that in the "supersaturated" system, that part of the silver and chromate which is not present in supersaturated solution, is combined with the gelatin, and that there is no appreciable separation of the solid phase, even in a highly colloidal form.

Inhibitive Action of Gelatin.—According to the well-known theory of von Weimarn, 16 the initial velocity of condensation of the molecules to form crystallisation centres may be formulated thus,

$$W=K\frac{\text{Condensation pressure}}{\text{Condensation resistance}}=K\frac{\mathcal{Q}-L}{L}=K\frac{P}{L}=Ku,$$

where W is the initial velocity of condensation, K is a constant, Q the total concentration of the substance which is to precipitate, L the solubility of coarse crystals of the substance, and Q-L=P the amount of supersaturation. The ratio P/L=u, which is the degree of supersaturation at the instant condensation begins, is thus taken as a measure of the tendency of the substance to separate in the solid state.

It seems reasonable to suppose that the inhibitive power of the gelatin is proportional to the tendency to precipitate in its absence and, as a first approximation, to formulate the degree of supersaturation in a manner analogous to the above by putting  $\mathcal Q$  equal to the concentration

<sup>\*</sup> The values of  $a_{\rm Ag^+}$  given under c and d in Table VI., are derived on the basis of the first alternative.

<sup>&</sup>lt;sup>18</sup> Von Weimarn, Kolloid-Z., 2, 199, 1908, etc.; 3, 3, 1908, etc.; 4, 27, 1909; Grundzuge der Dispersoidchemie, 1911; Zum Lehre von dem Zustanden der Materie, 1914.

of free silver (i.e., not combined with gelatin) in the "supersaturated" system and L equal to that in the corresponding "saturated" system. Values of Q, L, and u are shown in Table IX. The concentration of free silver in the "supersaturated" systems were derived from the e.m.f. values in Table IV. (c) by employing the graph obtained by plotting the e.m.f. values for aqueous solutions of silver nitrate against the concentrations of the latter (data in Table I.). The concentrations of free silver in the "saturated" systems were taken as equal to the activities (e, Table VI.).

TABLE IX.—Values for Degree of Supersaturation in Mixtures of Silver Nitrate, Potassium Chromate, and Gelatin.

₽ <sub>H</sub> .	Conc. of Gelatin. (Per Cent.)	Q. (×10³.)	L. (×10³.)	Degree of Supersaturation. $(u.)$	
					Mean.
5.7	0·46 1·34	0·95 1·10	0·112 0·105	7·5 9·5	8.5
5.3	0.10	0·70 1·10	0·118 0·124	4·9 7·9	9·1
"	I·22 I·69	1.30	0·118 0·124	10·0 9·5	0.0
5.0 ,, 4.8–4.9	0.49 1.18 0.47	1·55 1·80 1·55	0·133 0·180 0·141	9·0 10·0	9.9
4·7	1.16	1·95 0·85	0·214 0·123	8·1 5·9	
,, ,,	0·42 1·19	1·80 2·10	0.202	7·9 6·1	7·0 6·3
4·3 ,,	0·32 0·91 1·49	2·45 3·10 3·85	0·302 0·475 0·477	7·1 5·5 7·1	<b>₹</b> 3

It will be seen that at a given  $p_{\rm H}$  the value of u is roughly constant for systems with a gelatin content lying between 0.32 and 1.69 per cent. At some lower concentration it must decrease, since in the absence of gelatin the degree of supersaturation is nil. It therefore appears that, as might be expected, there is a critical concentration beyond which the inhibiting action becomes independent of the amount of gelatin present. This is consonant with the view that the gelatin acts by virtue of its tendency to be adsorbed by the incipient crystallisation centres, since there must be an upper limit to the adsorption.

The mean value of u given in the last column in Table VIII. is in each case the mean of the values for the above range of gelatin concentrations. According to these figures, the inhibitive action increases slightly as the  $p_{\rm H}$  decreases from 5.7 to 5.0, and then falls off more rapidly as the  $p_{\rm H}$  is further decreased. It was observed that at  $p_{\rm H}=5.0$  the gelatin solutions were very turbid compared with solutions at the other  $p_{\rm H}$  values. Kraemer 17 has also observed a very pronounced maximum in the Tyndall effect at  $p_{\rm H}=5.0$ , and suggests that the true isoelectric point of gelatin lies at this value. At the present stage it is not possible to do more than point out that there may be some connection between the inhibitive effects and the scattering phenomena.

<sup>&</sup>lt;sup>17</sup> Kraemer, "Colloid Symposium Monograph," 4, 102, 1926.

Findlay and King <sup>18</sup> found that a gelatin solution which had been heated and then suddenly cooled, affected the evolution of carbon dioxide from supersaturated solution to a more marked degree than when the gelatin was slowly cooled. This suggested that the "sol" form of the gelatin was responsible for the action on the gas. In the present work the gelatin was dispersed by heating at 35° C. for fifteen minutes, and added immediately to the salt solutions (at room temperature). The resulting mixtures were then kept at 25° C. for a few minutes before the final mixing. It would seem that these conditions should favour the "gel" form of the gelatin, as certainly must the waiting period of 72 hours at 25° C. In any case, the procedure was kept uniform throughout the work.

#### Summary.

Measurements of the activity of the silver ion in suitable systems show that :—

(I) in aqueous mixtures of silver nitrate and potassium chromate, containing sufficient gelatin to prevent precipitation in 72 hours, a portion of the silver chromate is present in the form of a highly supersaturated solution;

(2) gelatin combines with both silver and chromate ion, and that such combination accounts for that portion of the silver chromate in the above mixtures which is not present as simple ions;

(3) for a given  $p_{\rm H}$  the degree of supersaturation, and therefore the inhibitive action of the gelatin, probably becomes constant at some low concentration of gelatin;

(4) the inhibitive action of gelatin probably has an optimum value at  $p_{\rm H}=5$  o.

The authors' thanks are due to Imperial Chemical Industries Ltd., and to the Earl of Moray Endowment for assistance in the purchase of apparatus, and to Mr. Bruce, of Messrs. Cox Ltd., for the gelatin.

Department of Chemistry, King's Buildings, University of Edinburgh.

18 Findlay and King, J.C.S., 105, 1297,1914.

#### REVIEWS OF BOOKS.

The Conductivity of Solutions. By CECIL W. DAVIES, D.Sc. Second edition. Revised and enlarged. London, 1933. Chapman & Hall. Pp. viii + 281. 32 illustrations. Price 15s. net.

The fact that a second edition of Dr. Davies' book should have been called for after the lapse of three years from its first publication, is a testimony both to the wide interest taken in the subject-matter, and to the excellence of its presentation.

The book gives a clear exposition of the fundamental ideas and results underlying the modern development of the theory of conductivity in electrolytes, and a detailed and complete account of its experimental examination. Much work on the latter has been done during the last three years, and this has necessitated a large extension and a slight rearrangement of the subject matter. Two new chapters dealing with the practical applications of conductivity measurements have been added.

The reviewer has noted in particular the following additions. In the chapter on experimental methods there is a critical discussion of the use of the oscillator, and a detailed account of Schiele and Wien's use of the "baretter" bridge. Recent work of Gronwall, La Mer and others on effects arising from finite ionic diameters is repeatedly referred to. A very full discussion, that is particularly interesting in view of the author's own contributions to the subject, is given in Chapter XVIII. of the relative positions of the "physical" as compared with the chemical "dissociation constant" method of treatment of conductivities. In this connection great interest attaches to the discussion earlier in the book of the agreement between the theoretical slope "A" of the Debye and Hückel activity formula with recent determinations, and particularly with the results calculated from conductivity measurements on the basis of partial dissociation-Much new work on conductivities in non-aqueous solvents, and on the solva. tion of ions is included. Corresponding with the considerable amount of work that has been done in the last three years on deviations from Ohm's law at high frequencies, and in powerful fields, this subject has been treated in greater detail. The deduction of the existence of an effect of this kind on the basis of the theory of complete dissociation by the reviewer in 1923 is referred to. The chapter on conductimetric analysis has been extended so as to give a very clear and complete, though brief account of this method. Perhaps it may be pointed out that the improvement recommended by the author on page 240, in which the use of a special dial resistance box is advocated, may be enhanced by exchanging the position of the variable with that of the adjacent fixed resistance. A table of reciprocals then becomes unnecessary. The reviewer has for some time utilised an ordinary post office dial resistance box in this way, using the two fixed resistances as one, and employing a second titration vessel as the third resistance.

The new edition represents so large an extension of the former one, that it will have to be used by those who wish to have the most recent information on the subjects dealt with. The price has remained unaltered.

Die Technische Elektrolyse Wässeriger Lösungen. (Handbuch der Technischen Elektrochemie). Vol. II., Part I. By VICTOR ENGELHARDT. (Leipzig: Akademische Verlagsgesellschaft, M.B.H., 1933. Pp. 451. Price 42 M., bound 44 M.)

The earlier volumes of this series have been devoted to the metals and the present section comprises the production of hydrogen and oxygen by electrolysis and the preparation of alkalis and chlorine. A monograph entitled Electrolysis of Water is contributed by G. Pfleiderer and occupies a total of 196 pages. extent of the industrial application of this system of producing hydrogen and oxygen may be gauged by the fact that a space of forty-five pages is devoted to a noteworthy classification of recent patents on this type of electrolytic cells. An introductory section is devoted to theoretical aspects of electrolytic reactions and the main work deals with the construction of cells, diaphragms, and other components which are described and illustrated in detail, and data are given on all factors affecting the efficiency, economy, and performance of the plants and the durability of materials. The advance of hydrogenation processes is reflected in the large number of cells designed to yield the gases at high pressures. In these types, a number of different devices are described for safeguarding against the danger arising from the intermixing of the gases. Data of theoretical interest are given on the influence of pressure on power consumption and overvoltage. Descriptions of the processes to which these large developments in electrolytic gas production are applied are not entered into in this work but tabulated lists are given of the undertakings employing electrolytic gases in different countries. The main application of electrolytic hydrogen is seen to be for the synthetic production of ammonia and the outlet next in magnitude is to fat-hardening processes.

A section entitled Electrolysis of Aqueous Alkali Solutions is contributed by J. Billiter and F. Fuchs, under the sub-headings of processes with (I) separate outputs of chlorine and alkali; (2) rigid horizontal cathodes; (3) rigid cathodes without diaphragms; and (4) mercury cathodes. A detailed classification of patent literature is given and occupies 41 pages. A final section is devoted to the treatment of the final products and includes processes for liquefaction of chlorine, evaporation of alkali, preparation of bleaching powder and the production of hydrochloric acid from its elements.

The high standard of thoroughness of the earlier parts is maintained in this volume, particularly in the useful numerous diagrams and illustrations. The value of these publications to industrial interests may be considered to justify their substantial price, though this will place them beyond the individual reach of most students.

I. N. P.

Die Bedeckungstheorie der Passivität der Metalle und ihre experimentelle Begründung. By W. J. Müller. (Verlag Chemie, G.M.B.H., Berlin.) 102 pages, 65 figures and 31 tables.

Our present knowledge of anodic passivity is very largely based on the systematic researches carried out in the laboratory of Professor W. J. Müller at Vienna.

Hitherto, a student wishing to refer to this work has been compelled to consult a long series of papers published in an Austrian periodical, which is not available at every library. There have been some useful surveys published by Müller in the Zeitschrift für Elektrochemie, and a lecture printed in the Transactions of the Faraday Society; but a somewhat fuller account would seem to be

needed by any reader desirous of forming an independent judgment regarding the conclusions reached. This is the more necessary, since, although Müller's main contentions have obtained fairly wide acceptance, considerable discussion has arisen on certain points, notably with Güntherschulze, Smits, E. Müller and Tronstad. As long as Müller's argument remains split up in a large number of separate papers, the student must find a genuine difficulty in judging the validity of the conclusions.

For this reason, the present work, which sets forth in logical order the method, the experimental results and the interpretation, is greatly to be welcomed. The matter is essentially the same as that contained in the separate papers, but the author has taken the opportunity to introduce numerous small improvements. Consequently, although the nature of the subject makes the volume hardly suitable for light reading, any serious student of the book will agree that it is a wellexpressed statement of the position. Possibly some would desire further details of the experimental method, but it would have been only too easy to burden the text with small details which the majority of readers are prepared to leave to the experimenter. The derivation of the fundamental equations, notably those representing the Flüchenbedeckungsgesetz and the Tiefenbedeckungsgesetz, is clearly set forth, and the experimental evidence for the validity of these and other equations is concisely expressed in numerous curves and tables. The amount of quantitative experimental data included in the book is very large. There are also numerous photomicrographs, many of which have been taken by polarised light and represent the doubly refracting substances whose separation upon the metallic surface is the first step in the process which ultimately leads to passivity.

The book is essentially an account of the work in the Vienna laboratory, although researches conducted elsewhere are alluded to in a sympathetic manner; to the investigations of Hedges, which in some degree cover the same ground, there is a brief but appreciative reference. The experimental work described is, however, essentially of a co-operative character, in which numerous collaborators have taken part. Here the researches of Konopicky and Machu deserve first mention, but it may be interesting to note in the list the names of more than one young Englishman, who has been attracted to work in the pleasant atmosphere of the Wiener Technische Hochschule.

The general character of Professor Müller's argument is concisely expressed in his *Schlusswort*. "Starting," he writes, "from the observation that anodic passivation is a time-phenomenon, we have been led by systematic experimental and theoretical work to the *Bedeckungstheorie* of Passivity. We have seen that this theory is capable of explaining rationally some very complicated phenomena of passivity. It is to be noted that the whole theory in no way depends upon special assumptions, but is based entirely on Faraday's law, Ohm's law, Hittorf's law and Nernst's theory of electrode potentials." As regards the main phenomena explained by the theory, the average reader will probably feel that the claim for the absence of special assumptions is justified; if so, it is a point in favour of Professor Müller's views to which some of his critics have not always done justice.

U. R. E.

## LIQUID CRYSTALS AND ANISOTROPIC MELTS.

#### A GENERAL DISCUSSION.

THE FIFTY-EIGHTH GENERAL DISCUSSION organised by the FARADAY SOCIETY Was devoted to "Liquid Crystals and Anisotropic Melts."

On the 24th and 25th April, 1933, a meeting for the discussion of the above subject was held, by the courtesy of the Managers, in the Lecture Theatre of the Royal Institution. About 150 members and visitors were present. The President of the Society, Dr. N. V. Sidgwick, F.R.S., occupied the Chair throughout the meeting.

At the opening session Sir William Bragg, O.M., F.R.S., on behalf of the Managers of the Royal Institution, welcomed the Society and expressed their wishes for the success of the Society's deliberations.

The President then referred briefly to the lamented death of Geheimrat Professor F. Rinne, whose paper would be discussed later at the meeting. Those present stood in silence for some moments in memory of the Geheimrat.

The President then introduced the overseas members and guests individually to the Society and called upon them to rise in their places whereupon they were welcomed with acclamation by the Society. Those so welcomed were: Professor Dr. R. Schenck (Berlin), President of the Deutsche Bunsen-Gesellschaft, Professor D. M. Bose (Calcutta), Dr. W. Eisenschimmel and Frau Eisenschimmel (Prag), Professor K. Herrmann (Berlin-Charlottenburg), Professor R. O. Herzog (Berlin), Professor G. van Iterson (Delft), Dr. W. Kast (Freiburg), Professor L. S. Ornstein (Utrecht), Professor F. Paneth (Königsberg), Professor Dr. D. Vorländer and Dr. H. O. Vorländer (Halle a. Salle), Professor H. Zocher and Frau Zocher (Prag).

The Secretary then read messages of regret at their inability to be present from Professor C. W. Oseen, Professor V. Freedericksz, Professor W. Ostwald, Professor G. Foëx, Professor G. W. Stewart, Professor J. J. Trillat, Professor H. Mark, and from the immediate Past President, Sir Robert Mond.

After Professor Oseen's Introductory Paper had been taken as read and discussed, very beautiful experimental demonstrations were given by Professor Vorländer, Professor van Iterson and Dr. A. S. C. Lawrence. Further experimental demonstrations were given on Tuesday by Professor van Iterson and Mr. Bernal.

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The social headquarters of the meeting were, by kind invitation of the Executive Committee, at the Chemical Club, Whitehall Court, the

Society's lady guests being entertained at Whitehall Court.

Members of Council and English contributors of papers met the overseas guests informally for luncheon at Whitehall Court before the meeting commenced, and the Society entertained its overseas guests at dinner at Kettners' Restaurant on Monday evening.

At the conclusion of the meeting votes of thanks were accorded to the overseas guests for their presence and assistance in the success of the meeting; to Sir William Bragg and the Managers of the Royal Institution for their hospitality, and to Mr. Green and his assistants and other officers of the Royal Institution for their hospitality during the meeting; to the Committee of the Chemical Club for their hospitality; to the contributors of papers; to the organising committee (the President, Mr. Bernal and Mr. Rawlins), and to the translators of papers. In conclusion Professor Vorländer expressed the thanks of the overseas guests to the President and the Society.

The contributions, which had all been circulated in advance, were taken as read, the authors each devoting a few minutes to indicating the lines upon which they hoped their contributions would be discussed. The contributions will be found in the succeeding pages. The printed arrangement of the papers does not exactly follow the order in which they were presented at the meeting, since it was found that the General Discussion tended to classify certain of the papers in a different order. The General Discussion is reported at the end of the volume (p. 1060 onwards) in the order in which it was found convenient at the meeting.

### THE THEORY OF LIQUID CRYSTALS.

By C. W. OSEEN.

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In my monograph "Die anisotropen Flüssigkeiten, Tatsachen und Theorien" Fortschritte der Chemie, physikalischen Chemie und Physik. Bd. 20, 1929, I have among other things given a review of the results to which my theory had led by that time. The object of this article is to give a review of the results arrived at later on. In this connection I shall also enter upon some questions still unsolved.

#### 1. On the Forces that give Rise to Liquid Crystals.

As far as I know, the physicists who have paid attention to liquid crystals have all taken it for granted that the forces which cause molecules to combine so as to form a liquid crystal, are not the chemical valence forces, but belong to the large group of molecular forces. This assumption has been verified by Vorländer, whose statements are based upon the examination of a very large amount of chemical material. Now, as is well known, Debye and others have shown that the molecular forces may to a large extent be interpreted as electrostatic forces between the different nuclei and electrons that constitute molecules. Under these circumstances the question arises whether the forces between the molecules of a liquid crystal can also be supposed to be of an electrostatic nature. In my opinion the answer to this question must be negative.

Hitherto it has been possible in the theory of liquid crystals to ascribe to molecules rotational symmetry about an axis. For the determination of the positions and orientations of two molecules with regard to a definite co-ordinate system, then, ten quantities are needed. These may be, for either molecule, the three co-ordinates of the centre of gravity and the two angles that fix the direction of the axis of symmetry. Now there are  $\infty^6$  equivalent co-ordinate systems. From this it follows that the positions of the two molecules in relation to each other must be determined by four quantities. These quantities may be chosen as the distance between the centres of gravity  $(r_{12})$ , the cosine of the angle that the axis of symmetry of the first molecule, when drawn in a given direction, forms with the line joining the centres of gravity, drawn from molecule I to molecule 2, the cosine of the angle that the axis of symmetry of the second molecule, when drawn in the same direction, forms with the line of connection just mentioned, drawn from molecule 2 to molecule I, and the cosine of the angle that the two axes of symmetry form with each other. If by  $\mathbf{r}_{12}$  is meant the vector that is directed from the centre of gravity of molecule 1 to that of molecule 2, and if by  $L^{(1)}$  (or  $L^{(2)}$ ) is

<sup>&</sup>lt;sup>1</sup> D. Vorländer, Chemie der kristallinen Flüssigkeiten. Z. Kristallographie, 79, 64.

meant a vector of unit length which has the same direction as the axis of symmetry of the molecule I (or 2), then these quantities will be:

$$r_{12}$$
,  $\mathbf{L}^{(1)} \cdot \frac{\mathbf{r}_{12}}{r_{12}}$ ,  $\mathbf{L}^{(2)} \cdot \frac{\mathbf{r}_{21}}{r_{21}}$ ,  $\mathbf{L}^{(1)}\mathbf{L}^{(2)}$  . (1)  
 $(\mathbf{r}_{21} = -\mathbf{r}_{12})$ .

It is at once obvious, however, that these four quantities do not yield a single-valued determination of the positions of the two molecules relative to each other, but only a two-valued. The angle between the two planes which cut one another along the line joining the two centres of gravity and which contain each one of the two axes of symmetry, is determined as to its magnitude, but not with regard to its sign. For a single-valued determination of the positions of the two molecules relative to one another a further quantity is necessary, and this may be chosen to be:

$$\mathbf{L}^{(1)} \times \mathbf{L}^{(2)}$$
.  $\frac{\mathbf{r}_{12}}{r_{12}}$  . . . (2)

The square of this quantity, but not the quantity itself can be rationally expressed in the quantities (I). Accordingly it is only the sign of this quantity that introduces anything new.

From this it will be seen that there are two different kinds of liquid crystals. On the one hand there is a group characterised by the fact that the potential energy of two molecules may be expressed as a uniform function of the four quantities (I). On the other hand there is a group in the case of which such a description of the potential energy of two molecules is not possible, whereas this energy may be expressed as a uniform function of the four quantities (I) and of the quantity (2). It is one of the most important results of the theory, that the last-mentioned group of liquid crystals is identical with the group of cholesterinenematic substances. From this must be inferred that the molecular forces that give rise to liquid crystals, are of such nature that the potential energy of two molecules may depend on the sign of the quantity (2); in other words, of such nature that it may occur that the potential energy of two molecules is not invariant for a reflection at a plane in space. This requirement excludes electrostatic forces. Electrostatic energy, which depends only on the distances between the charges, cannot change when the whole system is reflected at a plane, since at this reflection all charges and all distances remain unchanged.

If the force between two molecules in a liquid crystal of the cholesterine-nematic type cannot be regarded as purely electrostatic, then it will be an obvious conclusion that the non-electrostatic part of the potential energy of two molecules is of a magnetic nature. This theory is corroborated by the fact that the magnetic force actually has a directing effect upon anisotropic molecules. From the point of view of atomic theory, too, there are reasons to believe that two molecules can, among other things, also exert magnetic forces on each other. If a molecule has an axis of symmetry, the total moment of momentum of the molecule, which is composed of the mechanical moment of momentum and the spin-moment of the electrons, must have a component along the axis of symmetry, which for every state with a fixed energy value has also a fixed value. In the case of liquid crystals only those states are at present taken into consideration where the moment of momentum coincides with the axis of symmetry. Evidently two molecules con-

structed in this way will exert magnetic forces on each other. On closer examination, however, it becomes evident that even in this way we do not obtain a satisfactory interpretation of the molecular forces that appear in liquid crystals. A moment of momentum along the axis of symmetry may, so far as the physical effects are concerned, to a first approximation be substituted by a magnetic moment in the direction of the axis of symmetry. According to the interpretation sketched above the cholesterine-nematic substances must necessarily be paramagnetic. But, so far as we know, this is not the case. Besides, even in that case we should not be any nearer the solution of the problem. For magnetostatic energy, like electrostatic, is invariant for reflection at a plane.

We have seen that, according to the theory, cholesterine-nematic substances are characterised by the fact that the potential energy of two molecules is not invariant for reflection. This agrees well with Vorlander's proposition that cholesterine-nematic substances are always so constructed that the molecule contains at least one asymmetric carbon atom.<sup>2</sup> Now, as is well known, the asymmetric carbon atom is characterised by optical rotary power. There naturally arises the question whether this effect does not suggest where the solution of the problem is to be found. Now the theories of optical rotary power that were started at the same time by M. Born and myself, both show that the essential fact here is the difference of phase that will exist between the different vibrators of the active molecule. It may be asked, then, whether the finite velocity with which the force is transmitted does not effect the interaction between two molecules. If we imagine two molecules which contain electrons rotating about axes in them, the interaction between them may, to a first approximation, be described by means of electric and magnetic dipoles, quadrupoles, and so on. But in an exact description the finite velocity of propagation of the force must also be taken into consideration. Here it is possible to understand how, in the case of cholesterinenematic substances, the potential energy of two molecules can undergo a change on reflection at a plane. If this is correct, the solution of the problem of liquid crystals is to be found in a chapter of atomic physics that is still unwritten.

#### 2. On Singularities of Structure in Nematic Substances.

If we suppose that the force between two molecules decreases rapidly enough as the distance increases, and if further we suppose that the density of the substance considered is constant, we shall find that the laws holding for the orientation of the axes of the molecules may be summed up in the requirement that an expression of the form

will have an extreme value. In the case of nematic substances  $K_{12}=0$ ,  $K_{22}=K_{33}$ . In this case we obtain a solution:

$$\begin{split} \mathbf{L}_1 &= \cos \phi, \ L_2 = \sin \phi, \ L_3 = 0, \\ \phi &= \frac{K_1 x_3}{2(K_{11} - K_{33})} + f(x_1, \ x_2), \\ \frac{\partial^2 f}{\partial x_1^2} &+ \frac{\partial^2 f}{\partial x_2^2} = 0.^3 \end{split}$$

<sup>&</sup>lt;sup>2</sup> Loc. cit., p. 84.

<sup>&</sup>lt;sup>3</sup> Cf. my above-mentioned monograph, Die anisotropen Flüssigkeiten, p. 49.

If we put:  $f=\pm\psi+\text{constant},\ \pm\frac{1}{2}\psi+\text{constant},\ \psi=\tan^{-1}\frac{x_2}{x_1}$ , we obtain structures with a single line  $x_1=x_2=0$ , which must optically show the phenomena described by Lehmann under the names of whole Kernpunkte  $(+\psi)$ , whole Konvergenzpunkte  $(-\psi)$ , half Kernpunkte  $(+\frac{1}{2}\psi)$ , half Konvergenzpunkte  $(-\frac{1}{2}\psi)$ . But as pointed out in the before-mentioned monograph, the theory also meets with difficulties. The energy of such a structure would be infinitely great, and, besides, it seems difficult to see why structures of the type:

$$f = k \log r$$

should not also be found.

We obtain a solution of these difficulties, if we abandon the assumption that the density is constant. Obviously the theory thus obtained will be far more complicated than before, and the formulæ are indeed so long that they cannot be reproduced here. For the new theory it is a matter of vital importance that the thermodynamic function which is to take a minimum value is the free energy. The entropy of an æolotropic substance is not known empirically. According to the theory every state of an element characterised by the distribution of the axes of the molecules in the different directions in space has its entropy. What is here to be taken into consideration, is, however, the most probable distribution and the entropy corresponding to this. Per unit of mass this entropy may be expressed as a function of the density and the absolute temperature  $F(\rho, T)$ . Hence we may write:

$$S = \int F(\rho, T) \rho d\omega$$
.

If we develop this theory by the methods of mathematical physics, we shall obtain a system of three differential equations for the determination of the direction of the axis and of the density. If we specially want to examine plane structures, i.e., structures in which, for instance,  $L_3=0$ , and  $L_1$  and  $L_2$  only depend on  $x_1$ ,  $x_2$ , the equations are reduced to two. In order that these equations may represent a nematic substance it is necessary to impose certain conditions on the coefficients. If we do so and put  $L_1=\cos\phi_1$   $L_2=\sin\phi$ , we obtain for the determination of  $\phi$  and  $\rho$  the equations:

$$\begin{split} \varDelta\phi &-\frac{\mathrm{I}}{\rho}\Big(\frac{\partial\phi}{\partial x_1}\frac{\partial\rho}{\partial x_1}+\frac{\partial\phi}{\partial x_2}\frac{\partial\rho}{\partial x_2}\Big)=0,\\ C_2{}^{(0)}\varDelta\rho &+2C{}^{(0)}\rho +2K_{22}\rho\Big[\Big(\frac{\partial\phi}{\partial x_1}\Big)^2+\Big(\frac{\partial\phi}{\partial x_2}\Big)^2\Big]=\beta+2m^2T\Big(F(\rho,T)+\rho\frac{\partial F}{\partial\rho}\Big). \end{split}$$

Obviously these equations may be satisfied by putting

$$\phi = k\psi, \, \psi = \tan^{-1}\frac{x_2}{x_1}, \, \rho = f(r) = f(\sqrt{{x_1}^2 + {x_2}^2}).$$

For the determination of the function f we obtain an ordinary differential equation of the second degree. For this differential equation r=0 is a singular point. By means of successive approximations we can find a solution of this equation which fulfils, for r=0, the conditions f=0, f'=0. Our system of equations has, however, no solutions of the form  $\phi=k\log r, \ \rho=f(\psi)$ . The two above-mentioned difficulties inherent in the theory of the singularities of structure of nematic substances, are thus removed.

A singular line in a nematic substance, the direction of which coincides with that of view, gives rise to a *Kernpunkt* or *Konvergenspunkt* and so

forth. If its direction is perpendicular to the direction of view, it gives rise to other phenomena. It appears, then, that we have to distinguish two cases. It may occur that the image of the singular line is on both sides surrounded by a half-shade, owing to the fact that one of the two rays in the aeolotropic substance, to which the incident ray has given rise, undergoes a deviation in the neighbourhood of the singular line, which prevents it from penetrating into the microscope. It may, however, also occur that there appears no such half-shade. These facts give rise to the question whether the difference between singular lines with a half-shade and such lines without a half-shade has any connection with the distinction between whole Kernpunkte, whole Konvergenzpunkte, half Kernpunkte, half Konvergenzpunkte. In order to solve this problem the author has made a geometrical-optical examination of the progress of the rays in the vicinity of a singular line. The result of this examination is that in all these cases the extraordinary ray undergoes a deviation in the vicinity of the singular line, but that this deviation is generally small, if the singular line is of the type "whole Kernpunkt" ( $\phi = \psi +$ Konst.), whereas it is always great, if the singular line belongs to any of the other types. Though this result is to be received with a certain reserve, as the methods of geometrical optics are not applicable when a ray undergoes sharp deviations, yet it seems probable that a singular line without a half-shade is always of the type "whole Kernpunkt"  $(\phi = \psi + \text{Konst.})$ , and that a singular line with a half-shade is in general of another type than this.

## 3. On the Iridescent Structures of Cholesterine-nematic Substances.

A substance, for which  $K_{12}=0$ ,  $K_1\neq 0$  has a tendency to appear in a structure that may be characterised as helicoidally-twisted. Mathematically such a structure may be described by means of the simple formulæ:

$$L_1 = \cos \alpha x_3, L_2 = \sin \alpha x_3, L_3 = 0.$$

Here **L** is as usual a vector of unit length which indicates the direction of the molecular axis. In my monograph and in the discussion arranged by Professor Ewald and published in *Z. Kristallographie*, I have given some information on the remarkable optical qualities of such structures. Here I shall give a more detailed account.

If the dielectric coefficient is regarded as a tensor with the components

 $\epsilon_{jk} = (\epsilon_3 - \epsilon_1)L_jL_k + \delta_{jk} \epsilon_1(\delta_{jk} = 0, if j \neq k, = I, if j = k)$ Maxwell's equations takes the form:

$$\mathrm{rot}\;\mathbf{H} = \frac{\epsilon_3 - \epsilon_1}{c} \Big(\mathbf{L} \frac{\partial \mathbf{E}}{\partial t} \Big) \mathbf{L} + \frac{\epsilon_1}{c} \; \frac{\partial \mathbf{E}}{\partial t}, \;\; \mathbf{rot}\; \mathbf{E} = - \; \frac{\mathbf{I}}{c} \; \frac{\partial \mathbf{H}}{\partial t}.$$

We consider first the solutions of these equations that correspond to waves propagated in the direction of the  $x_3$  axis. It appears that these solutions find their simplest expressions if, in addition to the fixed  $x_1$ ,  $x_2$  axes, we introduce a moving  $(x_1', x_2')$  system so chosen that the  $x_1'$  axis has at every point the same direction as the vector  $\mathbf{L}$  and that, consequently, the  $x_2'$  axis is perpendicular to  $\mathbf{L}$  and to the  $x_3$  axis. We put:

$$\begin{split} &\frac{\mathrm{I}}{2} \bigg[ \alpha^2 + \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \bigg] = a, \quad &\frac{\mathrm{I}}{4} \bigg[ \alpha^2 - \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \bigg]^2 - \frac{\omega^4}{16c^4} (\epsilon_1 - \epsilon_3)^2 = b, \\ &\Omega_1 = \sqrt{a + \sqrt{b}} + \sqrt{a - \sqrt{b}}, \quad \Omega_2 = \sqrt{a + \sqrt{b}} - \sqrt{a - \sqrt{b}}, \end{split}$$

and prescribe that, if b>0, in which case  $\Omega_1$  and  $\Omega_2$  are real, the roots shall be taken with their positive values, and, if b<0, in which case  $\Omega_1$  is real and  $\Omega_2$  purely imaginary, the signs shall be so chosen that  $\Omega_2$  takes the form -ki  $(k\geq 0)$ , whereas the real part of  $\Omega_1$  is still positive. If then we put:

$$-\Omega_1 = \Omega^{(1)}, -\Omega_2 = \Omega^{(2)}, \Omega_1 = \Omega^{(3)}, \Omega^2 = \Omega^{(4)}$$

we obtain the following expressions for the components of the strengths of the electric and the magnetic fields in the moving system just mentioned.

$$\begin{split} E_{1}{'} &= \frac{\mathrm{I}}{2} \bigg[ (\Omega^{(j)} + \alpha)^2 - \frac{\omega^2 \epsilon_1}{c^2} \bigg] e^{i(\omega t + \Omega^{(j)} x_3)}, \\ H_{1}{'} &= \frac{i}{2} \bigg[ \frac{c}{\omega} (\Omega^{(j)} + \alpha)^2 (\Omega^{(j)} - \alpha) + \frac{\omega}{c} (\epsilon_1 \alpha - \epsilon_3 \Omega^{(j)}) \bigg] e^{i(\omega t + \Omega^{(j)} x_3)}, \\ E_{2}{'} &= \frac{i}{2} \bigg[ (\Omega^{(j)} + \alpha)^2 - \frac{\omega^2 \epsilon_3}{c^2} \bigg] e^{i(\omega t + \Omega^{(j)} x_3)}, \\ H_{2}{'} &= -\frac{\mathrm{I}}{2} \bigg[ \frac{c}{\omega} (\Omega^{(j)} + \alpha)^2 (\Omega^{(j)} - \alpha) + \frac{\omega}{c} (\epsilon_3 \alpha - \epsilon_1 \Omega^{(j)}) \bigg] e^{i(\omega t + \Omega^{(j)} x_3)}. \end{split}$$

A discussion of these expressions already gives valuable information on the strange optical qualities of helicoidally-twisted strata. If b > 0, which occurs, if  $\omega$  lies outside the interval  $c\alpha/\sqrt{\epsilon_1}$ ,  $c\alpha/\sqrt{\epsilon_3}$ , all  $\Omega^{(j)}$ , as observed are real. Our formulæ show that in this case there are two elliptically polarised waves in either direction. Their velocities of propagation are  $\omega/\Omega_1$  and  $\omega/\Omega_2$ . During the propagation the ellipse of vibration rotates thus that its principal axes always fall along the  $x_1'$  and  $x_2'$  axes. If, on the contrary, b < 0, that is, if  $\omega$  lies within the interval  $c\alpha/\sqrt{\epsilon_1}, c\alpha/\sqrt{\epsilon_3}, \Omega_2$  and consequently  $\Omega^{(2)}$  and  $\Omega^{(4)}$  are purely imaginary. The corresponding waves are, referred to the moving co-ordinate system, to be taken as standing waves. These waves, too, are elliptically polarised so that the principal axes of the ellipse of vibration fall along the  $x_1$ and  $x_2$  axes. The amplitude increases, for the wave [4], exponentially with  $x_3$ . For the wave [2] the amplitude decreases exponentially with  $x_3$ . Within the interval  $c\alpha/\sqrt{\epsilon_1}$ ,  $c\alpha\sqrt{\epsilon_3}$  there will generally be a region where  $kd \gg 1$ , d being the thickness of the zeolotropic stratum. This region is called the interior part of the interval. In this part of the spectrum there is then a wave the upper amplitude of which is enormous compared to the lower, and another wave the lower amplitude of which is enormous compared to the upper. The above-mentioned propositions are of fundamental importance for the study of the reflection of a wave in a cholesterine-nematic stratum of iridescent structure, and of its passage through this stratum. Let us imagine that a wave that comes from the region  $x_3 < 0$ , meets the æolotropic substance in the plane  $x_3 = 0$  and leaves it in the plane  $x_3 = d$ . The requirement that in the plane  $x_3 = d$  there shall be no incident radiation, gives rise to two linear connections between the vector components  $E_1(d)$ ,  $E_2(d)$ ,  $H_1(d)$ ,  $H_o(d)$ . Let us now specially consider a wave that may in the interior of the substance be represented by the formulæ:

$$\begin{split} E_{1}{'} &= \sum_{j=1,\ 2,\ 4} A_{j} \frac{\mathrm{I}}{2} \bigg[ (\Omega^{(j)} + \alpha)^{2} - \frac{\omega^{2} \epsilon_{1}}{c^{2}} \bigg] e^{i(\omega t + \Omega^{(j)} x_{3})}, \\ E_{2}{'} &= \sum_{j=1,\ 2,\ 41} \frac{\mathrm{I}}{2} \bigg[ (\Omega^{(j)} + \alpha)^{2} - \frac{\omega^{2} \epsilon_{3}}{c^{2}} \bigg] e^{i(\omega t + \Omega^{(j)} x_{3})}. \end{split}$$

The conditions just mentioned, applicable to  $x_3=d$ , make it possible to express  $A_1$  and  $A_4$  in the forms  $A_2e^{-kd}F_1(\alpha,\omega,C,\epsilon_1,\epsilon_3)$  and  $A_2e^{-kd}F_2(\alpha,\omega,C,\epsilon_1,\epsilon_3)$ , respectively. Hence it will be seen that  $A_1$  and  $A_4$  belong, roughly speaking, to the same order of magnitude as  $A_2e^{-kd}$ . In the interior of the interval  $c\alpha/\sqrt{\epsilon_1}$ ,  $c\alpha/\sqrt{\epsilon_3}$  they are infinitesimal compared to  $A_2$ . Hence in the vicinity of the plane  $x_3=0$  we obtain with very great accuracy:

$$E_1' = A_2 \frac{1}{2} \left[ (\alpha - \Omega_2)^2 - \frac{\omega^2 \epsilon_1}{c^2} \right] e^{i\omega t - kx_3}.$$

From these expressions for  $E_1{}'$ ,  $E_2{}'$ ,  $H_1{}'$ ,  $H_2{}'$  we can now determine the corresponding expressions  $E_1{}^{(i)}$ ,  $E_2{}^{(i)}$ ,  $H_1{}^{(i)}$ ,  $H_2{}^{(i)}$  for the incident wave, as well as the components  $E_1{}^{(r)}$ ,  $E_2{}^{(r)}$ ,  $H_1{}^{(r)}$ ,  $H_2{}^{(r)}$  of the reflected wave. In both cases we obtain comparatively simple expressions showing that both waves are elliptically polarised. We can also determine the components,  $E_1{}^{(g)}$ ... of the wave coming from the plane  $x_3=d$ . It appears, as may also be concluded from what is said above, that the amplitude of this wave bears to that of the incident wave a proportion of the order of magnitude  $e^{-kd}$ : I. The incident wave thus undergoes a total reflection, when it meets the æolotropic stratum.

It is interesting to examine more strictly the expressions for the incident and the reflected wave. We refer them, of course, to the fixed  $(x_1, x_2, x_3)$  system. In order to obtain the simplest possible formulæ we put:

$$E_1^{(i)}+iE_2^{(i)}=E_1^{*(i)},\quad E_1^{(i)}-iE_2^{(i)}=E_2^{*(i)},$$

and in the same way:

$$H_1^{(i)} + iH_2^{(i)} = H_1^{*(i)}, \quad H_1^{(i)} - iH_2^{(i)} = H_2^{*(i)}.$$

We have in these denominations:

$$\begin{split} E_1^{*(i)} &= -iH_1^{*(i)} = \frac{\omega}{4c} (\epsilon_3 - \epsilon_1) \Big( \frac{\omega}{c} - \alpha + \Omega_2 \Big) A_2 e^{i\omega(t - z_3/c)}, \\ E_2^{*(i)} &= iH_2^{*(i)} = \frac{c}{2\omega} \Big[ (\alpha - \Omega_2)^2 - \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \Big] \Big( \frac{\omega}{c} + \alpha + \Omega_2 \Big) A_2 e^{i\omega(t - z_3/c)}, \\ E_1^{*(r)} &= iH_1^{*(r)} = \frac{\omega}{4c} (\epsilon_3 - \epsilon_1) \Big( \frac{\omega}{c} + \alpha - \Omega_2 \Big) A_2 e^{i\omega(t - z_3/c)}, \\ E_2^{*(r)} &= -iH_2^{*(r)} = \frac{c}{2\omega} \Big[ (\alpha - \Omega_2)^2 - \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \Big] \Big( \frac{\omega}{c} - \alpha - \Omega_2 \Big) A_2 e^{i\omega(t - z_3/c)}. \end{split}$$

The quantities  $\Omega^{(j)}$  (j = 1, 2, 3, 4) are roots of the equation:

$$\Omega^4 - 4a\Omega^2 + 4b = 0.$$

This equation may also be written:

$$\left[(\alpha-\Omega)^2-\frac{\omega^2}{2c^2}(\epsilon_1+\epsilon_3)\right]\left[(\alpha+\Omega)^2-\frac{\omega^2}{2c^2}(\epsilon_1+\epsilon_3)\right]=\frac{\omega^4}{4c^4}(\epsilon_3-\epsilon_1)^2.$$

If  $\Omega_2$  is purely imaginary, it follows that

$$\left|\frac{\frac{\omega^2}{2c^2}(\epsilon_3-\epsilon_1)}{(\alpha+\Omega_2)^2-\frac{\omega^2}{2c^2}(\epsilon_1+\epsilon_3)}\right|=1.$$

There is then such a number  $t_0$  that:

$$\begin{split} \frac{\omega^2}{2c^2}(\epsilon_3 - \epsilon_1) &= \left[ (\alpha + \Omega_2)^2 - \frac{\omega^2}{2c^2}(\epsilon_1 + \epsilon_3) \right] e^{-it_0} \\ &= \left[ (\alpha - \Omega_2)^2 - \frac{\omega^2}{2c^2}(\epsilon_1 + \epsilon_3) \right] e^{+it_0}. \end{split}$$

On account of this our expressions for  $E_1^{\star(r)}$  and  $E_2^{\star(r)}$  may be written:

$$\begin{split} E_1^{\bullet(r)} &= \frac{c}{2\omega} \bigg[ (\alpha + \Omega_2)^2 - \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \bigg] \Big( \frac{\omega}{c} + \alpha - \Omega_2 \Big) A_2 e^{i\omega(t - t_0 + z_3/c)}, \\ E_2^{\bullet(r)} &= \frac{\omega}{4c} (\epsilon_3 - \epsilon_1) \Big( \frac{\omega}{c} - \alpha - \Omega_2 \Big) A_2 e^{i\omega(t - t_0 + z_3/c)}. \end{split}$$

If we write  $E_1^{(i)}$  and  $E_2^{(i)}$ :

$$\begin{split} E_1^{(i)} &= R\{ae^{i\omega(t-x_3/c)+i\alpha}\} = a\cos\{\omega(t-x_3/c)+\alpha\}, \\ E_2^{(i)} &= R\{ibe^{i\omega(t-x_3/c)+i\beta}\} = -b\sin\{\omega(t-x_3/c)+\beta\}, \end{split}$$

 $E_1^{(r)}$  and  $E_2^{(r)}$  will take the form:

$$\begin{split} E_1^{(r)} &= R\{ae^{i\omega(t-t_0+x_3/c)-i\alpha}\} = a\cos\{\omega(t-t_0+x_3/c)-\alpha\},\\ E_2^{(r)} &= R\{-ibe^{i\omega(t-t_0+x_3/c)-i\beta}\} = b\sin\{\omega(t-t_0+x_3/c)-\beta\}. \end{split}$$

The formulæ for  $E_1^{(r)}$  and  $E_2^{(r)}$  will be transformed into the formulæ for  $E_1^{(i)}$ ,  $E_2^{(i)}$ , if  $t_0-t$  is substituted for t. This proves that the ellipses of vibration of the incident and the reflected wave have exactly the same form and the same size. With regard to the different directions of propagation it also shows that in both cases the vibration, regarded by an observer towards whom the wave advances, takes place in the same direction. There is then no difference between the two waves but the opposite directions of propagation and a difference of phase.

We have found that there exists a wave of light, elliptically polarised in a given manner, which is subjected to a total reflection in the helicoidally twisted structure, at which reflection the reflected wave has, but for a difference of phase, exactly the same character as the incident wave. In order to master the problem of reflection we must also take another wave into consideration. We obtain it by examining a wave which in the æolotropic substance is determined by the formulæ:

$$E_{1}' = \sum_{j=1,3,4} B_{j} \frac{1}{2} \left[ (\Omega^{(j)} + \alpha)^{2} - \frac{\omega^{2} \epsilon_{1}}{c^{2}} \right] e^{i(\omega t + \Omega^{(j)} x_{3})},$$

$$E_{2}' = \sum_{j=1,3,4} B_{j} \frac{1}{2} \left[ (\Omega^{(j)} + \alpha)^{2} - \frac{\omega^{2} \epsilon_{3}}{c^{2}} \right] e^{i(\omega t + \Omega^{(j)} x_{3})}.$$

In this case I shall only mention the result of the computation. We put:

With this notation we have:

$$\begin{split} E_1^{\star(i)} &= \frac{\omega}{4c} (\epsilon_3 - \epsilon_1) \Big\{ \Big( \frac{\omega}{c} + \alpha \Big) N_1 - \Omega_1 N_2 \Big\} B_4 e^{i\omega(t - x_3/c)}, \\ E_2^{\star(i)} &= \frac{c}{2\omega} \Big\{ \Big[ \Big( \frac{\omega}{c} + \alpha \Big) \Big( \alpha^2 - \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \Big) + \Big( \frac{\omega}{c} - \alpha \Big) \Omega_1^2 \Big] N_1 \\ &\quad + \Omega_1 \Big[ \frac{2\alpha\omega}{c} - \alpha^2 + \Omega_1^2 - \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \Big] N_2 \Big\} B_4 e^{i\omega(t - x_3/c)}, \\ E_1^{\star(r)} &= \frac{\omega}{4c} (\epsilon_3 - \epsilon_1) \Big\{ \Big( \frac{\omega}{c} - \alpha \Big) N_1 + \Omega_1 N_2 \Big\} B_4 e^{i\omega(t + x_3/c)}, \\ E_2^{\star(r)} &= \frac{c}{2\omega} \Big\{ \Big[ \Big( \frac{\omega}{c} - \alpha \Big) \Big( \alpha^2 - \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \Big) + \Big( \frac{\omega}{c} + \alpha \Big) \Omega_1^2 \Big] N_1 \\ &\quad + \Omega_1 \Big[ \frac{2\alpha\omega}{c} + \alpha^2 - \Omega_1^2 + \frac{\omega^2}{2c^2} (\epsilon_1 + \epsilon_3) \Big] N_2 \Big\} B_4 e^{i\omega(t + x_3/c)}. \end{split}$$

For the wave that emerges from the plane  $x_3 = d$  we finally obtain:

$$\begin{split} E_{1}^{\star(g)} &= \frac{\epsilon_{3} - \epsilon_{1}}{2\alpha(\epsilon_{1} + \epsilon_{3} - 2)} (\Omega_{1}^{2} - \Omega_{2}^{2}) \Big(\frac{\omega}{c} + \alpha + \Omega_{2}\Big) B_{4} e^{i\omega(t - x_{3}/c) + i\alpha d}, \\ E_{2}^{\star(g)} &= - (\Omega_{1}^{2} - \Omega_{2}^{2}) \Big\{ \mathbf{I} + \frac{\mathbf{I}}{2\alpha} \Big(\frac{\omega}{c} + \alpha + \Omega_{2}\Big) \\ &- \frac{c^{2}}{\omega^{2}\alpha(\epsilon_{1} + \epsilon_{3} - 2)} \Big(\frac{\omega}{c} + \alpha + \Omega_{2}\Big) \Big[ \Big(\frac{\omega}{c} + \alpha\Big)^{2} - \Omega_{1}^{2} \Big] \Big\} B_{4} e^{i\omega(t - x_{3}/c) - i\alpha d}. \end{split}$$

From these formulæ it will be seen that if a plane wave, advancing in the direction of the normal, meets a helicoidally-twisted structure, the intensity of the reflected wave as well as that of the passing one must in general be a periodic function of  $\Omega_1$ . d. Now, if the two bounding surfaces of the æolotropic substance are not exactly parallel, but form a small angle, then both in the reflected light and in that which has passed there will appear dark stripes at constant distances from one another, all parallel to the line of intersection of the bounding surfaces. If, however by means of an elliptical polariser we cause the incident ray to be of the first type considered above, these dark stripes will not appear. The conclusions here drawn from the theory agree perfectly with the observations that have been made with relation to the so-called stripes of Grandjean. It cannot very well be assumed that this agreement is due to a mere chance. There will then be no reasons why the so-called planes of Grandjean should really exist.

We have mentioned above some consequences of the theory which agree with known facts. I shall now point out some consequences, the correctness of which is questionable. According to the statements of our experimentalists, the iridescent structures of cholesterine-nematic substances have an optical rotary power which in certain cases is very great. Now the above formulæ show that in the interior of the region  $c\alpha/\sqrt{\epsilon_1}$ ,  $c\alpha/\sqrt{\epsilon_3}$ , there is no optical rotary power in the usual sense of the word. Every wave which, having passed through the æolotropic stratum, emerges from the plane  $\chi_3=d$ , must be obtainable through a linear combination of those emergent waves that correspond to the two types of elliptically polarised waves in the structure. We know, however, that the former type, which gives rise to a total reflection, does not give any perceptible wave emergent from the plane  $\chi_3=d$ . The ellipse of

vibration of the wave that emerges from this plane has then exactly the same form, and the principal axes of this ellipse have exactly the same directions, whatever the incident wave may be. Hence a rotary power in the usual sense of the word is out of the question. As we see, the argument stated here is based on the existence of an elliptically polarised wave that on incidence in the substance is subjected to a total reflection. Now this consequence of the theory agrees with facts. Then it seems probable that the conclusion that has here been drawn from this consequence, also agrees with facts. According to Friedel the optical rotary power actually changes its sign for a certain wave-length, taking then an infinitely large value. But in the place of the spectrum where this infinite rotary power was supposed to be found, no rotation at all can be shown, because, according to Friedel, the emergent wave is circularly polarised. If we leave Friedel's theory of the infinitely great rotary power out of the question and keep to what can be directly observed. the theory seems to agree with facts on this point too.

We shall now leave the region  $c\alpha/\sqrt{\epsilon_1}$ ,  $c\alpha/\sqrt{\epsilon_3}$  and consider the parts of the spectrum for which  $\omega$  falls outside this interval. The result of the theory is that in these regions of the spectrum there is no rotary power in the usual sense of the word. It is true that an incident, planepolarised wave that passes through the stratum, is changed into an elliptically-polarised wave whose greater axis of vibration forms an angle with that of the incident wave, but this angle does not depend linearly on the thickness of the stratum, but in a far more complicated way. If, as the experimentalists state, the iridescent structure of a cholesterinenematic substance really has an optical rotary power of the usual kind, then, on this point, the theory in its present state disagrees with facts. It must be added, however, that our experimentalists seem to have taken it for granted that, when a rotation of the plane of polarisation is perceptible, there will also be a rotary power in the usual sense of the word. A careful examination of phenomena of this kind is at present one of the most pressing needs with reference to liquid crystals.

An account has been given of the laws which hold for the perpendicular incidence of a wave in the iridescent structure of a cholesterine-nematic substance. But it is also very interesting to study the reflection and refraction of a non-perpendicular wave. It is found empirically that, in the case of a non-perpendicular wave also, there is a region in the spectrum in which a component of the wave undergoes a total reflection. As the incidence of the wave becomes oblique instead of perpendicular, the region of total reflection is displaced towards the violet part of the spectrum. It is this fact, above all, which the theory has to explain. The investigation shows that an incident wave, for which the components of the electromagnetic field are proportional to:

$$e^{i\omega\left(t-rac{eta_1\chi_1+eta_2\chi_2+eta_3\chi_3}{c}
ight)}$$
 (where  $eta_1^2+eta_2^2+eta_3^2=1$ )

gives rise to a wave of the type:

$$E_{j} = e^{i\omega\left(t - \frac{\beta_{1}\chi_{1} + \beta_{2}\chi_{2}}{c}\right)} e^{\frac{i\hbar\omega\chi_{3}}{c}} F_{j}(\chi_{3}),$$
(where  $j = 1, 2, 3$ ).

The functions  $F_i(x_3)$  are periodic with the period  $2\pi/\alpha$ . They satisfy the conditions:

$$F_{j}\left(x_{3}+\frac{\pi}{\alpha}\right)=-F_{j}(x_{3}).$$

h is a transcendent function of c,  $\omega$ ,  $\alpha$ ,  $E_1$ ,  $E_3$  and  $\beta^2 = \beta_1^2 + \beta_2^2$ . In order that a total reflection may occur, it is necessary that h should have a complex value. This is, as we know, the case for  $\beta = 0$  if  $\omega$  falls in the interval  $c\alpha/\sqrt{\epsilon_1}$ ,  $c\alpha/\sqrt{\epsilon_3}$ , i.e., if the wave-length lies within the limits:

$$\frac{2\pi}{\alpha}\sqrt{\epsilon_1}$$
 and  $\frac{2\pi}{\alpha}\sqrt{\epsilon_3}$ .

Now, if  $\beta^2 > 0$  but so small that  $\beta^4$  may be neglected compared with unity these limits will be displaced to:

$$\frac{2\pi}{\alpha}\sqrt{\epsilon_1}-\beta^2$$
 and  $\frac{2\pi}{\alpha}\sqrt{\epsilon_3-\beta^2\frac{\epsilon_1+\epsilon_3}{2\epsilon_1}}$ .

We see that the theory explains why the displacement takes place towards the side of the short waves. Besides the region of total reflection, which remains for the case of  $\beta=0$ , there is, however, an infinite number of other such regions. They all lie on the violet side of the region first found. Now, if we pass from perpendicular incidence to oblique, it will not only occur that the region of reflection already present is displaced towards the violet part of the spectrum, but new colours will appear on the violet side of this region.

One of the most remarkable properties known as to the iridescent structures of cholesterine-nematic substances, is the fact that their colour depends both on the angle that the incident light forms with the normal and on that which the reflected light forms with this normal. By this it seems that one of the oldest optical laws which exists, namely that according to which the angle of reflection is determined by the angle of incidence and equal to this, does not hold for these structures. The theory developed does not explain this fact. A theory of it may, however, be given, which is based upon the properties of helicoidally-twisted strata. We only have to remember that no body has an absolutely plane surface and that, if two plane surfaces existed, it would never be possible to adjust them so as to be perfectly parallel to each other. From this it follows that the theory concerning the iridescent strata of cholesterine-nematic substances must also take into account the case where a bounding surface divides the structure obliquely, so that the preparation takes the form of a wedge. In this case other phenomena will appear. If, for the sake of simplicity, we assume the stratum to be infinitely thick, the most important result of the theory can be expressed as follows: A plane polarised wave incident on the plane bounding surface of a helicoidally twisted stratum, the normal of which makes an angle with the axis of the stratum, gives rise to a reflected wave, which is composed of an infinite number of plane waves with different directions of propagation. The relation between the angle of incidence and that of reflection is therefore not single-valued. An infinite number of angles of reflection correspond to a given angle of incidence.

#### 4. On the Motion of Æolotropic Liquids.

It has been known for some long time that many liquids do not move in accordance with the Navier-Stokes equations of motion. In 1925 Kruyt summed up the investigations then made and arrived at the result that disperse-systems with globular particles follow the law given by Poiseuille which holds for a liquid passing through a tube, whereas

deviations from this law appear in the case of systems with non-spherical particles. Further material since 1925 has confirmed the correctness of Kruyt's conclusion. Under these circumstances Dr. A. Anzelius 4 set himself the task of formulating laws of motion valid for a liquid with oblong molecules. We shall give below a survey of the theory of Anzelius and the results to which it has led hitherto.

Anzelius assumes that in a liquid consisting of oblong molecules with symmetry of rotation, the direction of the axis of a molecule will vary continuously from point to point, even if the liquid moves, so that at a certain moment there will be a certain direction of axes for every element of volume. Under these circumstances we can no longer suppose that Navier's and Stoke's assumptions concerning the tensor of viscosity

$$\tau_{jk} = - p \delta_{jk} + \mu \left( \frac{\partial u_j}{\partial x_k} + \frac{\partial u_k}{\partial x_j} \right)$$

holds good. Instead, we must assume that this tensor will depend also on the direction of the axis of the molecule, *i.e.*, on L. On the presumption that a dissipation-function exists, Anzelius determines the form of this function. His results may be summed up in the statement that the dissipation function, F, must have the form:

where 
$$\begin{split} A_1 \sum_{\substack{j,k = \\ 1,2,3}} D_{jk}^2 + A_2 \sum_k \Bigl(\sum_j L_j D_{jk}\Bigr)^2 + A_3 \Bigl(\sum_{j,k} L_j L_k D_{jk}\Bigr)^2 \\ &+ 2A_4 \sum_{j,k} L_j L_k D_{jk} \sum_m D_{mm} + A_5 \Bigl(\sum_m D_{mm}\Bigr)^2, \end{split}$$

and  $A_1 \ldots A_5$  are constants. From F we obtain the tensor of viscosity by the formulæ:

$$\tau_{jk} = -p\delta_{jk} + \frac{1}{2} \frac{\delta F}{\delta D_{jk}}.$$

Now the question arises, how the directions of the axes of the molecules are to be determined. Anzelius assumes that between the molecules there are forces in action that have rotary moments about the centres of gravity. The analytical expression for these forces he takes from the present author's theory of liquid crystals. But he assumes further that the motion of the liquid has a directive effect on the molecules. This, he supposes, is due to the fact that on account of the motion the impacts of the molecules give rise to a rotary moment. Taking the conditions of symmetry for his basis he finds for this moment, **M**, an expression, which may be written in the form:

$$\begin{split} \mathbf{M} &= \{ (\mathcal{C}_1 - \mathcal{C}_2)(\mathbf{L}D) + \frac{1}{2}(\mathcal{C}_1 + \mathcal{C}_2)(\mathbf{L} \times \text{rot } \mathbf{u}) \\ &+ (\mathcal{C}_{11} + \mathcal{C}_{12})(\mathbf{L} \times (\mathbf{L}D)) - \frac{1}{2}(\mathcal{C}_{11} - \mathcal{C}_{12})\text{rot } \mathbf{u} \} \times \mathbf{L}. \end{split}$$

 $C_1$ ,  $C_2$ ,  $C_{11}$ ,  $C_{12}$  are constants. (**L**D) is the vector whose components are  $L_jD_{j1}$ ,  $L_jD_{j2}$ ,  $L_jD_{j3}$ . Here, a term in which the same index appears twice, will, with regard to this index, be summed up over the values I, 2, 3.

Finally I should mention the boundary condition which Anzelius introduces into his theory. He assumes that, in a flowing liquid, asymmetrically constructed molecules arrange themselves perpendicularly to the wall.

<sup>4</sup> A. Anzelius, Über die Bewegung der anisotropen Flüssigkeiten. The Annual of the University of Uppsala, 1931.

Basing our computations on these assumptions we may now proceed to calculate the motion of a liquid in given cases. As appears from what is said above, one of the most interesting cases is that of a liquid flowing through a tube, because in this case a liquid with oblong molecules does not give the same result as a liquid with spherical molecules. Anzelius summarises the results of his calculations on this case as follows:

- I. The theoretical relation between the pressure gradient and the amount of liquid passing per unit of time agrees with the experimental relation, if  $A_3 < 0$ .
- 2. When  $A_3$  is negative, the distribution of velocity over the transverse section of the tube is different from that found in the case of isotropic substances, in that the velocity in the middle of the tube is comparatively greater. Ostwald supposes, though he cannot refer to any theory or observations, that in flowing æolotropic liquids an equalisation of the velocities will take place in the transverse section, analogous to that which occurs in turbulent isotropic liquids. The result arrived at does not agree with Ostwald's assumption.
- 3. The orientation of the molecules depends on the sign of the pressure gradient, that is, on the direction of the flow. This agrees with an observation by Professor R. Fåhreus, Uppsala, according to which blood that is absorbed by a capillary, seems to change its colour, when the direction of the flow is reversed.
- 4. As the velocity of the flow increases, the molecules tend to take a direction which is parallel to the axis of the tube. This phenomenon is analogous to the rotation of the molecules in electric and magnetic fields, which may, if the field strength is sufficiently high, cause the destruction of the edge stratum.

Anzelius has further investigated the behaviour of an æolotropic liquid in the case of Couette's arrangement, that is, when the liquid is enclosed between two coaxial cylinders, the inner of which is stationary, whereas the outer one rotates with constant velocity round the common axis. If the inner radius is  $r_1$  and the outer one  $r_2$  if  $(r_2-r_1)/r_1=E$ , and if  $\omega$  is the angular velocity of the outer cylinder, and  $M_d$  is the rotary moment acting per unit of length on the inner cylinder, he finds:

$$M_d = \alpha \omega + \beta \omega^3$$

where:

$$\alpha = \frac{2\pi A_1 r_1 r_2}{2E - E^2 + E^3}, \quad \beta = \frac{\pi A_3 C_2^2 r_1^3 r_2^3}{60 K_{22}^2} E \text{ for asymmetrical molecules,}$$
 or 
$$= \frac{\pi A_3 C_1^2 r_1^3 r_2^3}{60 K_{22}^2} E \text{ for symmetrical molecules.}$$

To this must be added an expression for the largest angle that the axis of a molecule forms with the radius vector from the axis of the cylinder:

$$\lambda_{\max} = \frac{C_2}{8K_{22}} r_1 r_2 \omega E.$$

We see that by determining  $\omega$ ,  $M_d$ ,  $\lambda_{\rm max}$ , we shall also be able to determine three constants  $A_1$ ,  $A_3$  and  $C_2/K_{22}$ .  $K_{22}$  is a constant taken from the author's theory of liquid crystals.

Anzelius has further investigated the manner in which, in Couette's case, the stability of the motion is affected by the æolotropy of the molecules. In order to make the complicate calculations possible he had to assume that the axis of a molecule adjusts itself radially everywhere.

The investigation is of interest, because in this case, too, one must assume

 $A_3 < 0.$ 

I hope that the above review of the theory of Anzelius has shown the great interest it deserves. Attention must, however, be called to a difficulty inherent in this theory. During the motion of a liquid the moment **M** has to do work. It is not clear how this work stands with regard to the principle of energy.

On account of these doubts as to the theory of Anzelius the author has developed another theory of the motion of an æolotropic liquid. According to this theory the state of an element is characterised by a vector **L**, whose components are the mean values of the unit vectors that indicate the directions of the axes of the molecules belonging to the element. Accordingly the direction of the vector **L** indicates the mean directions of the axes of these molecules. Its length indicates the æolotropy of the element. For the flow of the liquid and for the changes of the vector **L** the following laws can be formulated:

$$\begin{split} &\rho\frac{du_{j}}{dt}=X_{j}-\frac{\delta\rho}{\delta x_{j}}-\rho\frac{\partial}{\delta x_{j}}\!\!\int\!\!F(x,x',\mathbf{L},\mathbf{L}')dm'+\sum_{k}\frac{\partial\tau_{2k}}{\delta x_{k}},\\ &\rho d^{2}\frac{d^{2}L_{j}}{dt^{2}}=\Lambda_{2}+\rho A\frac{L_{j}}{a}-\rho\frac{\partial}{\delta L_{j}}\!\!\int\!\!F(x,x',\mathbf{L},\mathbf{L}')dm'-\sigma_{j}. \end{split}$$

Here  $X_j$  (j=1,2,3) are the components of the external force that acts on the liquid,  $\Lambda$ , are the components of a generalised external force, for instance the magnetic. A is a quantity characteristic of the theory and called the pressure of orientation.  $Fdm\ dm'$  is the potential energy of the element dm in the neighbourhood of the point x and of the element dm' in the neighbourhood of the point X'. In order to determine the tensor of viscosity  $\tau_{jk}$  and the corresponding vector  $\sigma$  we assume that they depend on a dissipation function  $G(D_{jk},\ dL_{j}/dt;\ \mathbf{L},\ \mathbf{rot}\ \mathbf{u})$  so that

$$\begin{split} \tau_{jk} &= \frac{\Im G\Big(D_{jk}, \frac{dL_j}{dt}; \ \mathbf{L}, \ \mathbf{rot} \ \mathbf{u}\Big)}{\Im D_{jk}}, \\ \sigma_j &= \frac{\Im G}{\Im \frac{dL_j}{dt}}. \end{split}$$

The heat produced per unit of volume and unit of time is then 2G.

The two equations given above do not suffice to determine the motion. To them must be added the condition of continuity:

$$\rho \frac{dv}{dt} = \sum_{j} \frac{\partial u_{j}}{\partial x_{j}},$$

and the equation of the conduction of heat:

$$\rho T \frac{d}{dt} \frac{\partial \zeta}{\partial T} + 2G = \mathbf{div} \ \mathbf{j}.$$

Here  $v = I/\rho$  is the specific volume,  $\zeta$  the free energy, and j the current of heat. Further the equations of the state of the liquid must be added:

$$p = -\frac{\partial \zeta}{\partial v}, \quad A = -\frac{\partial \zeta}{\partial A}.$$

The theory expressed in these formulæ agrees with the principle of energy.

According to the opinions generally accepted it may be assumed that the dissipation function G is a homogeneous, quadratic function of the nine quantities  $D_{jk}$ ,  $dL_j/dt$  the coefficients may be functions of  $L_j$  and rot  $\mathbf{u}$ . A natural hypothesis enables us to determine G more closely. It is a plausible assumption that all forces of friction vanish, when the liquid moves like a solid body. This assumption is equivalent to the assumption that G is a homogeneous, quadratic function of the eight quantities  $D_{jk}$ ,  $\mathbf{L} \frac{d\mathbf{L}}{dt}$ ,  $\frac{d\mathbf{L}}{dt}$  rot  $\mathbf{u}$ . The coefficients may as before depend on  $\mathbf{L}$  and rot  $\mathbf{u}$ .

The theory sketched above has not yet been used for the calculation of given problems of motion. I have mentioned it here, because it seems to me to throw light upon one of Lehmann's most remarkable observations on liquid crystals. He found that in certain cases a substance, spread out between two glass surfaces, would be put into motion, when influenced by a flow of heat coming from below, during which motion the different drops of liquid seemed to be in violent rotation. Further investigations convinced Lehmann that in this case it was not the drop itself, but the structure, that moved. According to my opinion the observed motion was due to the fact, that the molecules rotated with the same speed round vertical axes drawn through their centres of gravity.

At this rotation  $\mathbf{u} = 0$ ,  $\mathbf{L} \frac{d\mathbf{L}}{dt} = 0$ . Consequently all forces of viscosity vanish. The "violent speed" is hereby explained.

#### 5. On the Forms of Liquid Crystals.

When Lehmann introduced the term "liquid crystals," he did it not only on account of the double refraction found in certain liquids, but also on account of the form that drops of certain substances, namely those which are now usually called the smectic ones, will take under favourable conditions. That this form is not spherical is the first important fact in this connection that a theory of liquid crystals has to explain. Lehmann's further investigations showed that smectic drops can assume a multitude of different forms, some of which are characterised by considerable grace and symmetry. To find these forms theoretically is the final object of the theory in this connection.

In my contribution to the discussion on liquid crystals arranged by Professor Ewald and published in Z. Kristallographie, I formulated a mathematical problem, the solution of which was calculated to throw light upon the above questions. Roughly speaking, it stands to the exact thermodynamic treatment of them as Laplace's theory of capillarity stands to Van der Waals' theory. The problem was formulated like this: It is required to determine a closed surface, S, a region outside it, S, and a vector function S which fulfils the condition S in the interior of S so that the expression:

$$\begin{split} \frac{\rho^{(a)^2}}{2m^{(a)^2}} & \{ K_{11} (\mathbf{L} \ \text{rot} \ \mathbf{L})^2 \times K_{33} ((\mathbf{L}\Delta)\mathbf{L})^2 \} d\omega \\ & \qquad \qquad + \frac{1}{2} \int_{S} \Big\{ \frac{\rho^{(a)^2}}{m^{(a)^2}} f_1(L_n) + \frac{2\rho^{(a)}\rho^{(i)}}{m^{(a)}m^{(i)}} f_2(L_n) + \frac{\rho^{(i)^2}}{m^{(i)^2}} G_2 \Big\} dS, \end{split}$$
 where 
$$\rho^{(a)}, \ \rho^{(i)}, \ m^{(a)}, \ m^{(i)}, \ K_{11}, \ K_{33}, \ G_2 \end{split}$$

are constants and K is the region enclosed by S, takes the smallest value that is compatible with the conditions:

$$\rho^{(a)} \int_{K} d\omega = Nm^{(a)}, \quad \rho^{(i)} \int_{U} d\omega = Mm;$$

N and M being here constant, positive numbers.

The above problem has been subjected to an investigation by Mr. N. E. Larsson. The following is for the most part based upon this in-

vestigation.

If we want to solve a problem in the calculus of variations, we may begin by formulating the necessary conditions to be fulfilled by the solution, which conditions follow from the requirement that a small variation of the wanted functions must leave unchanged the expression that is to take the minimum value. In the problem under consideration we can firstly vary the directions of the axes of the molecules, or in other words, the vector  $\mathbf{L}$ , and secondly the form of the crystal, in other words that of the closed surface S. Through the former variation we obtain the laws holding for the orientation of the molecules in a liquid crystal. These laws, which must of course agree with the laws ealier formulated by the author, have the form:

$$\begin{array}{l} [(K_{11}-K_{22})\{2 \ \mathbf{L} \ \mathrm{rot} \ \mathbf{L} \cdot \mathrm{rot} \ \mathbf{L} - \mathbf{L} \times \mathrm{grad} \ (\mathbf{L} \ \mathrm{rot} \ \mathbf{L})\} \\ + K_{33} \ \mathrm{rot} \ \mathrm{rot} \ \mathbf{L}] \times \mathbf{L} = 0 \end{array} . \quad (\mathbf{I})$$

Further we obtain a condition that must be fulfilled at the bounding surface S. If, for the sake of simplicity, we put:

$$\frac{m^{(a)^2}}{\rho^{(a)^2}} \Big\{ \frac{\rho^{(a)^2}}{m^{(a)^2}} f_1(L_n) + \frac{2\rho^{(a)}\rho^{(i)}}{m^{(a)}m^{(i)}} f_2(L_n) + \frac{\rho^{(i)^2}}{m^{(i)^2}} G_2 \Big\} = f(L_n),$$

this condition may be written:

$$(K_{11} - K_{33})L_n$$
. L rot L.L -  $K_{11}$  L rot L.n  
+  $K_{33}$   $L_n$ . rot L -  $\frac{1}{2}f'(L_n)$ . n  $\times$  L = 0 . (2)

The variation of the form of the crystal gives a new condition which the surface S must fulfil:

$$K_{11}(\mathbf{L} \text{ rot } \mathbf{L})^{2} + K_{33}((\mathbf{L}\Delta)\mathbf{L})^{2} + f'(L_{n})\operatorname{div} \mathbf{L} + \sin \psi \frac{df'(L_{n})}{dt} + \{f(L_{n}) - f'(L_{n}) \cdot L_{n}\}\left(\frac{1}{R_{1}} + \frac{1}{R_{2}}\right) = \operatorname{constant} = K \qquad (3)$$

Here  $\psi$  is the angle between the vector  $\mathbf{L}$  and the normal  $\mathbf{n}$  drawn outwards. df'/dt is the derivative of the function f' in the direction given by the projection of the vector  $\mathbf{L}$  on the tangent plane of the surface.  $R_1$  and  $R_2$  are the radii of curvature of the surface, taken as positive, if the corresponding centre of curvature lies within the surface S.

As the problem is difficult, it will be allowable to begin by investigating

simple cases.

It appears from Lehmann's photographs that one structure, which is at least approximately realised in many smectic drops, is so shaped that the axes of the molecules are parallel, and the form of the drop is determined by the fact that its bounding surfaces are a right circular cylinder and two planes perpendicular to this. The direction of the axes of the molecules coincides with the direction of the generatrices of the cylinder. Now the question arises whether this structure agrees with the theory developed.

It is at once obvious that the law holding for the structure of the interior of a liquid crystal, is fulfilled. The first boundary condition, too, is fulfilled, if we make the plausible assumption that f'(0) = 0. The second boundary condition is fulfilled by the cylindrical boundary surface. But it is not fulfilled with regard to the plane end surfaces, because the left-hand member of the equation (3) has the value 0, whereas the right-hand member must have the value K. From this it follows that our assumptions concerning this structure cannot all be correct. We see also where we shall have to make a correction. The assumption that the non-cylindrical bounding surfaces are plane, cannot be absolutely correct. From this follows that in the vicinity of these surfaces L cannot be a constant. If the end surfaces have a different form, for instance spherical, it will not be difficult to satisfy the equation (I) and the first boundary condition. This may be done thus, that the axes of the molecules are assumed approximately to fulfil the condition rot L = 0and to arrange themselves perpendicularly to the end surfaces. But the question still remains to be answered why these end surfaces are but slightly curved. We see, however, from our formula (3) that an explanation is afforded at once. If we apply this formula to the cylindrical bounding surface, we shall obtain f(0) as coefficient of the medium curvature. If, on the contrary, we apply it to the end surfaces, we shall obtain f(I). We only have to assume  $f(I) \gg f(0)$  and the approximately plane form of the end surfaces will be explained. It should be noticed that the assumption  $f(1) \gg f(0)$  is also necessary for the explanation of the prolate form that is characteristic of the smectic drops considered. The fact that the molecules at the greatest part of the bounding surface adjust themselves so as to be parallel to this surface, proves that  $f(I) \gg$ f(0). The theory thus traces the prolate form and the approximately plane end surfaces to a common origin.

Much work will yet be required before the strange and beautiful forms that smectic drops will often take are explained. But the framing of a theory of these forms has begun.

## I. REMARKS ON SYSTEMS WITH MIXED DIMENSIONS.

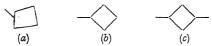
By D. Vorländer (Halle-a-S.).

Received in German on 18th January, 1933, and translated by Dr. E. Friedmann.

At the end of my paper on the "Chemistry of Crystalline Fluids," in the Zeitschrift für Kristallographie, I brought forward the proposition: "Perhaps the secret of liquid crystals remains not in their property of belonging to one, two or three dimensions, but in their mixed dimensionality, in which at least one dimension prevails, thus following the type of molecules, of which the crystalline-liquid order consists." I thought that this proposition was quite intelligible in the light of the preceding explanations, but soon I saw that the expression "mixed dimensional" sounded somewhat strange. The editor of this Zeitschrift für Kristallographie added a big interrogation mark!

#### 900 REMARKS ON SYSTEMS WITH MIXED DIMENSIONS

If one takes any universally limited surface and combines it with a straight line, also limited (where one accepts for reasons of simplicity that surface and line as lying in the same plane), one has a system, which has one and two dimensions. If the line and the surface belong not to the same plane, or where a body occupying space is added, the new system has not only one but two and three dimensions. Systems of this kind have not one or two or three dimensions, but they are of mixed dimensions. I asked my colleague who teaches mathematics, whether things of this kind were dealt with in an exact way, but I got a negative reply. "Such things are too complicated." And yet the chemist thinks in such systems and works with them, although he is obliged to make definite restrictions, according to the nature of the molecules and atoms. The more complicated case, for instance, a mixed dimensional system, consisting of a scalene plane quadrangle and a straight line, such as form (a), is scarcely to be found in chemistry. On the other hand, the simpler system consisting of a square and a line (in the plane of the square), as represented in Fig. (b), might occur.



If we imagine the line in (b) produced in the direction of the diagonal of the square, or if we add a new line continuing the first line in a straight direction, corresponding to Fig. (c), we get the possible special case, that the line predominates with its one dimension. We can transfer these considerations at once on the chemically important systems consisting of a regular hexagon and a line, demonstrated by benzene, where the predominance of the one dimension is obtained, either by producing the one line to the outside (d) or by combining the hexagon with two lines, which appear in the direction of the diagonal of the hexagon (e):



Both cases can be examined experimentally and are to be found having the same influence in numerous crystalline liquid benzene derivatives of definite form, for instance:

for (d) 
$$C_6H_5$$
 . CH : CH . CH : CH . CH . COOH ;  $^2$  for (e)  $pC_2H_5OOC$  . CH : CH .  $C_6H_4$  . N : CH .  $C_6H_4$  . CH : CH . COOC $_2H_5$ . $^3$ 

In the last example the system (e) occurs three times over in the form of a para-substituted benzene compound; in the same way (d) and (e) can easily be combined by linear addition of the hexagons. In spite of its extended surface crystalline-liquid derivatives of naphthalene can be prepared by the straight line 2, 6-substitution,

$$R \cdot CH : N - N : CH \cdot R \text{ (Naphthalene).}$$
 
$$R \cdot CH : N - N : CH \cdot R \text{ (Diphenyl).}$$

Ber. deut. chem. Ges., 62, 545, 1929; J. prakt. Chem. (2), 121, 247, 1929.
 Z. Krist., 79, 285, 1931.

and one easily sees by comparing these products geometrically with the corresponding diphenyl-derivatives that, in full agreement with experimental data, the latter are more definitely linear than the former. But on what experimental foundations can we follow these geometrical considerations? The linear effect is recognized by the increase or the decrease of the crystallinity through radical R.CH. If this is not substituted in the para-position (benzal, cinnamal) it can only change the strongly linear diphenyl derivative, but not the less markedly linear naphthalene derivative into the crystalline-liquid state. If the radical R. CH: is substituted in the para-position (p-tolylal, anisal, ethoxybenzal) the diphenyl-derivatives obtained become very strongly liquid crystalline (enantiotropy with large sphere of existence), the naphthalenederivatives feebly liquid crystalline (monotropy or enantiotropy with a smaller sphere of existence in the liquid-crystalline phase).

Twenty-five years ago I developed the theory that these elongated, rod-shaped "linear" molecules have a specially strong tendency to form liquid-crystalline phase.4 I succeeded in demonstrating how this theory allows one to prepare any number and any kind of liquid-crystalline substances, as well as in showing how these systems of mixed dimensions with one dimension predominating favour generally the formation of anisotropic crystals and consequently the formation of ordinary solid crystals. The predominant one-dimensional state is to be considered in spite of the recurring two- or three-dimensional state of the molecules or atoms, as one of the most important factors concerning the

formation and cohesion of anisotropic crystals.

In the movement of the systems the straight line gives the greatest stability in direction of movement, coinciding with the possibility of the closest parallel packing and order, and, thus, the strongest force field effect between the systems. This view does not exclude other factors; for instance, in the unsaturated groups and in the benzenederivatives, the specific associative character. The surfaces play their part also.

If we imagine now that a limited straight line cutting another straight line or meeting it in an angle, we obtain crosses, branches, or forks. Among these, as explained above, one dimension can be considered as predominating, when one of the two lines is long compared with the second. Examples of this kind can be found experimentally in any number. I ascertained that here, too, the liquid crystalline as well as the solid crystalline states are concerned. In one of the following papers I describe new liquid crystalline varnishes and glazes, which are derived from a cross-like naphthalene system.

One can show further, with regard to the crystalline effect of the ethyl radical —CH2—CH5—, that the longest straight carbon chain appears in this group of two carbon atoms. The prolongation in the direction of the tetrahedron angles gives rise in the case of the n-propyl radical, with three carbon atoms, to an obtuse angle and by that to

<sup>&</sup>lt;sup>4</sup> Ber. deut. chem. Ges., 40, 1970, 1907; 41, 2035, 1908; Krist. flüssige Substanzen, Enke, Stuttgart, 1908.

a crystalline decrease; and further in the case of n-butyl with its four carbon atoms, that on account of its parallel ended zigzag line, there is again a crystalline increase.5 The straight zigzag line composed of an even number of carbon atoms as well as the wave line or screw line with a straight axis may contain systems of mixed dimensions with predominating one-dimensionality. They are accessible to chemical experiments. Dr. K. Herrmann brings forward in his paper contributed to this discussion an example of a zigzag line in the liquid-crystalline thallo-salts of fatty acids, described by myself and R. Walter.<sup>6</sup> angles, rhombs, parallelepipeds, prisms and similar uniaxial forms, cannot at present be conceived in molecular chemistry.

The grouping of molecular models by geometrical diagrams is far from satisfactory. The benzene derivatives, with their surfaces and their straight line para-substituents, fall in with such a grouping better than by the branched carbon compounds with their bifurcated grouping. The "straight line" is very often nearly suppressed by the angular linking and by the hydrogen, oxygen, nitrogen etc. atoms, attached to the carbon atoms, which all co-operate with the carbon atom to produce a crystalline form. Yet in all ways the line can be readily distinguished. The X-ray experiments of K. Herrmann and Krummacher confirmed in general my views as to the parallel arrangement of rod-shaped molecules in liquid crystalline melts.

> <sup>5</sup> Z. physik. Chem., 126, 449, 1927. 6 Ber. deut. chem. Ges., 43, 3122, 1910; 59, 962, 1926.

### II. SUPRACRYSTALLINITY OF p-AZOXYBENZOIC ACID.

By D. Vorländer (Halle-a-S.).

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The ordered structure of a substance arises from a cooled disordered medley of mobile but equal building stones, which may predominate in an amorphous melt or solution of the substance; here already, and not at first in the finished crystal, do the building stones start to get more or less into touch with one another in accordance with their form and the stability of the direction of their movement. On the other hand, the crystalline structure is broken up by heating, at the meltingpoint, or by dissolution, and changes again, and the building stones are jumbled into a medley. In most cases the molecules, the building stones, are more stable to temperature than the crystals; in other words, the crystalline substance melts undecomposed. Frequently the crystalline substance melts with decomposition, the structure of the molecules begins to change simultaneously with the structure of the crystals or to break down completely. In other cases—and these have not up to the present been sufficiently appreciated—the crystalline substance does not melt at all; with rising temperature it can be destroyed completely without previously coming to fusion, for instance, at the decomposition or explosion of solid crystalline substances. When the molecular structure, thermodynamically considered, breaks down

more easily than the crystalline structure the molecules in the crystal are more strongly combined one with another than the atoms in the molecules: the highest possible degree of crystallinity.

Consider now p-azoxybenzoic acid or similar compounds, such as oxamide, fumaric acid, terephthalic acid, diphenyl-pp'-dicarbonic acid, cyclohexadiene-I, 4-dicarbonic acid and others, with their linear molecules as building stones. We can predict (from my theory as to the influence of linear molecules on crystallinity) that these compounds must very readily form anisotrope crystals, stable at high temperature, where neither the measure of rapidity of growth nor even the size of the crystals comes into question. At first sight these compounds do not seem to show "an extreme tendency towards crystallization." The p-azoxybenzoic acid forms an almost unfiltrable powder, nearly insoluble in all solvents, which cannot be melted, which every one, after careful microscopical investigation, would pronounce to be amorphous or, at the best, crypto-crystalline: "a substance of high molecular weight of frozen amorphism." I worked for a long time with such amorphous powders and formed finally the following opinion: these powders are not amorphous and not of high molecular weight, but on the contrary they are strongly crystalline and of a simple molecular weight.

The experimental grounds which lead to such strange results, contradicting the ordinary behaviour of powdered p-azoxybenzoic acid, are the following: p-axoxybenzoic acid can be converted into enantiotropic liquid-crystalline diethyl ester and diallyl ester, whose solid crystalline phases do not at all differ either in solubility or in molecular weight and melting-point from ordinary crystalline substances. In the same way the monoethyl ester of p-azoxybenzoic acid is crystalline liquid, and its solubility and crystallinity in the solid phase are normal. The crystalline liquid state of the esters demonstrates their strong crystallinity. Therefore free p-azoxybenzoic acid can be by no means amorphous, the more so in that in many other cases the free carbonic acids are more strongly crystalline than their esters. Thus, in solubility insolvents and the powdery condition of p-azoxybenzoic acid are not based on high molecular weight, but on the circumstance that the strained molecules of the acid are very strongly bound in the crystal (even at the moment of their formation by precipitation from alkaline solution with dilute hydrochloric or acetic acid) and leave no room in the intermolecular force-field for the molecules of the solvent. In this way the possible growth of crystals out of melt or solvent develops with solubility. P-azoxybenzoic acid carbonizes on heating without previously softening; its great stability at high temperatures, as in the cases of graphite or carbon, previously considered to be amorphous. 1 may be a sign of a high degree of crystallinity. An internal formation of compounds, somewhat in the sense of amine + acid  $\rightarrow$  salt, is very improbable in the case of azoxy acid, because the amino character of the azoxy compounds is very weak. An association of the carboxyl groups by no means leads in the case of benzoic acid as in acetic acid or in the angular aromatic dicarbonic acids (o- and m-phthalic acid, etc.), to substances which cannot be melted.

The question then arises whether the acid was really crystalline, as powder, supra-crystalline liquid or supra-crystalline solid. The answer was given by an X-ray investigation which Dr. E. Schiebold

<sup>&</sup>lt;sup>1</sup> See U. Hoffmann and D. Wilm, Z. physik. chem., 18B, 401, 1932.

in Leipzig was so kind to undertake. Two preparations of powdery p-azoxybenzoic acid, one dark yellow (a), the other light yellow (b), were put at his disposal. With the consent of Dr. Schiebold I bring forward the result of his investigation. "The light yellow and the dark yellow powders gave very similar diagrams. Both substances are crystalline. The clearly recognizable Debye-Scherrer rings required much longer exposure (three times) in the case of the light yellow substance than in that of the dark yellow material before they became apparent." The results of the measurements of the diagram are given in the following Table:—

Nr.	Dark Substance.			Light Substance.		
	α.	Sin a.	Int.	α.	Sin α.	Int.
1 2 3 4 5 6 7 8 9 10	8° 09' 12° 18' 13° 39' 15° 39' 18° 51' 20° 48' 25° 33' 28° 06' 32° 39'	0·1418 0·2130 0·2360 0·2697 0·3231 0·3551 0·4313 0·4710 0·5395	stst stst stst w m m-st m w	8° 15′ 12° 15′ 13° 48′ 15° 18′ 19° 09′ 20° 48′ 25° 15′ 27° 45′ 31° 51′ 40° 51′	0·1435 0·2122 0·2388 0·2639 0·3280 0·3551 0·4266 0·4656 0·5277 0·6541	stst stst stst w m-s m-st m w ww

DEBYE-SCHERRER DIAGRAM OF p-AZOXYBENZOIC ACID.\*

[ $\alpha$  = angle of reflection = d/2. Int. = intensity; stst = very strong; st = strong; mst = fairly strong; m = medium; w = weak; ww = very weak—only just recognisable.]

"The interference lines of the light yellow substance are noticeably broader than those of the dark material. Moreover, the lack of clarity of the inner rings in the former case is striking in comparison with their sharpness in the latter case. This seems to indicate that the particle size is smaller in the former case. Possibly also the shape of the crystallites in the two cases is not the same."

The diagrams show that powdered azoxybenzoic acid is solid crystalline and not liquid-crystalline.

Some data as to the origin of these substances are decidedly worthy of communication.

p-azoxybenzoic Acid.—The preparation of this substance was carried out by reducing p-nitrobenzoic acid with sodium arsenite.<sup>2</sup> From the aqueous and, if necessary, filtered solution of the separated sodium salt of azoxybenzoic acid the free azoxy acid is precipitated by an excess of dilute hydrochloric acid. In order to filter the acid and to wash it out, preparation (a) was boiled with dilute hydrochloric acid and preparation (b) was allowed to settle at room temperature and then centrifuged. Both preparations were dissolved once more in sodium carbonate solution, precipitated, filtered off and then washed for several days with hot water to which was added a few drops of dilute hydrochloric acid; finally they were digested with pure water and washed, until in the filtrate neither sodium nor chlorine ions, nor arsenic were detectable.

<sup>\*</sup> Communicated by Dr. E. Schiebold.

<sup>&</sup>lt;sup>2</sup> F. Meyer and K. Dahlem, Liebigs Ann., 326, 334, 1903.

The powders, which nevertheless still contained traces of sodium, were dried in vacuo at 110° and cooled.

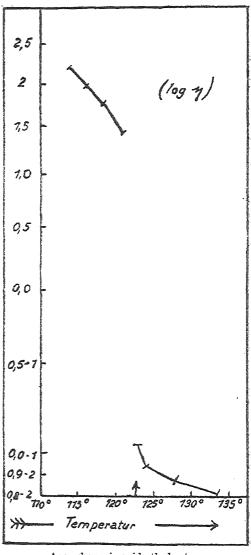
Strange to say, during the reaction with boiling thionyl chloride (10 g. acid and 75 c.c chloride) for forty to eighty hours the apparently finer light yellow powder (b) was attacked and dissolved with greater

difficulty than the darker yellow coarse preparation (a), although both were previously powdered as fine as dust. Azoxy acid can behave very differently with thionyl chloride, depending upon its during treatment washing drying. and After filtration of the thionyl chloride solution of unchanged azoxy acid and after distillation of the greater part of the excess chloride, p-azoxy= benzoyl chloride, on addition of petroleum ether, crystallizes in fine, matted yellow needles; it can be recrystallized from alcohol free chloroform and petroleum ether: melting-point 155°, not liquidcrystalline.

C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub> Cl<sub>2</sub>. Calc. 8·7 per cent. N; 22·0 per cent. Cl. Found 8·6 per cent. N; 21·1 per cent. Cl.

This acid chloride serves for the easy preparation of the ester of the azoxybenzoic acid, previously only obtained with difficulty, from the interaction of the silver salts with alkyl halide.<sup>3</sup>

Diethyl Ester of p-Azoxybenzoic Acid is formed by boiling the chloride with ten times



Azoxybenzoic acid ethyl ester.

its weight of absolute alcohol for four hours. If the ester contains azo compounds and appears reddish-yellow, the admixed azo ester can be oxidized to azoxy ester by heating it on the water bath with hydrogen peroxide in glacial acetic solution—pure yellow prismatic platelets;

<sup>&</sup>lt;sup>3</sup> Vorländer, Ber. deut. chem. Ges., 39, 804, 1906.

melting-point, I. 123-124°, II. 114°. It is an enantiotropic crystalline liquid and forms two crystalline solid phases. The different powdered azoxy acids (a) and (b) give the same diethyl and dimethyl esters (m.p. 206°; not crystalline-liquid). The determination of the viscosity  $\eta$  of the crystalline-liquid phase of the diethyl ester gave, according to the experiments of A. H. Krummacher, deviations from the earlier measurements of Eichwald.4 We visualized the presence of a second crystalline-liquid phase, but neither the viscosity nor the time-temperature curve showed a sufficiently large discontinuity to warrant the assumption of more than one crystalline-liquid phase. The variation in the viscosity during the change, amorphous liquid -> crystalline liquid is within I° to 2°, and, as seen on microscopical inspection without a cover glass, is accompanied by the formation of thickly packed, comparatively mobile pocks. The succeeding jump in the  $\eta$ -values on changing from amorphous liquid to crystalline liquid is very large; moreover, the quantity of heat developed by the azoxy ester goes with much greater discontinuation that in the case of the p-azoxyphenly

Diallyl Ester of p-azoxybenzoic Acid, prepared from acid chloride and pure allyl alcohol, is, at variance with earlier observations, an enantiotropic crystalline liquid (melting-point, I. 95-96°, II. 90°) and forms, just as the diethyl ester, pocks and little rods.

p-azoxybenzoic Acid Monoethyl Ester is formed by heating for two hours a solution of 6.3 g. diethyl ester (I mol.) in 300 c.c. absolute alcohol with 8.5 c.c. of 2.18 normal alcoholic sodium hydroxide (1 mol). The sodium salt of the ethyl acid ester, which separates on cooling the mixture in small light yellow crystals, is sucked off, dissolved in 200 c.c. of warm water, filtered from some undissolved, unsaponified ester and decomposed with cold 2 N hydrochloric acid. The acid ester crystallizes in light yellow needles and is, after washing with water, recrystallized from alcohol or acetone; readily soluble in acetone, soluble in hot glacial acetic acid and alcohol, it sinters at 257° and is decomposed at temperatures over 260° with discoloration and development of gas. Microobservation shows the crystalline-liquid phase (as a slimy oil), which, on further heating, melts, with partial decomposition to an amorphous liquid; on decreasing temperature the crystalline-liquid phase and the crystalline-solid phase come back; enantiotropic crystalline-liquid

 $C_{16}H_{14}N_2O_5$ : Calc. C, 61·2; H, 4·5; N, 8·9: Found C, 61·0; H, 4·0; N, 8·9. The same ester acid is obtained by half saponification of the diethyl ester with alcoholic alkaline lye at room temperature.

<sup>4</sup> Diss., Marburg, 1904.

### III. REMARKS ON LIQUOCRYSTALLINE RESINS AND LACQUERS,

By D. Vorländer (Halle-a-S.).

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We know that the solid crystals have every degree of hardness or softness; in the same way we shall recognize one day that the crystallineliquids can assume any imaginable degree of viscosity which might be conceived also as hardness.

I described the first representatives of liquid-crystalline resins together with Richard Wilke in the esters of arylidene p-amino cinnamic acid. and on the esters of allyl and acyl-p-oxyphenylazocinnamic acid.<sup>1</sup>

One can make a great number of liquid-crystalline resins of various kinds, starting from the fact that the crystallinity decreases by ramification and bifurcation of the molecules. If one goes too far with the ramification, one gets, in agreement with my theory, to more or less stationary super-cooled amorphous resins and lacquers; if, however, one retains in the molecules the predominance of one dimension, one obtains liquid-crystalline super-cooled resins and lacquers, which, as distinguished from the arylidene esters, are stable at room temperature.2 The crystalline liquids are here, as well as by some other properties,3 more closely related to amorphous melts than to solid crystals.

Anisal-1-aminonaphthalene-4-azobenzene.—The amorphous melts of this substance can be cooled with ice or by pouring it into a vessel with carbondioxide snow in order to get a plastic and adherent liquidcrystalline resin at room temperature. For many purposes it has the disadvantage that it can only be obtained from the amorphous melt in the monotropic form and solidifies as a crystal at room temperature in a few hours, and, in the warm, very quickly. X-ray diagrams could not be taken.

I tried, therefore, to make enantiotropic liquid-crystalline resins of great stability. If, however, one emphasizes more strongly the linear form in the geometrical system by introducing the azoanisole- or the azophenetole-radical instead of the azobenzene radical, the liquid-crystalline phases became enantiotropic and more strongly crystalline, but they cannot be super-cooled so readily to resins and lacquers. I took, therefore, for further syntheses the azobenzoic acid radical,4 and combined the aminoazo ester (in order to decrease the crystallinity) with the bifurcated p-N-dimethyl aminobenzaldehyde.

I prepared this new ester with Siegfried Baentsch in the following way:

Ethyl Ester of 1-aminonaphthalene-4-azobenzoic Acid.—25 g. paminobenzoyl-ethyl ester (Anæsthesine) are suspended in the warm

<sup>&</sup>lt;sup>1</sup> Ber., 41, 2046, 1908; R. Wilke, Diss., Halle, 1909.

<sup>&</sup>lt;sup>2</sup> Vorländer, Z. physik. Chem., 105, 246, 1923; Z. ang. Chem., 43, 13, 1930. <sup>3</sup> J. Fischer, Z. physik. Chem., 160A, 101, 1932.

<sup>&</sup>lt;sup>4</sup> See Ber., **63**, 2506, 1930.

in 250 c.c. 6 per cent. hydrochloric acid and while cooled with ice diazotized with the calculated amount of sodium nitrite (11·0 g. in 40 c.c. water). The filtered diazonium salt solution is added gradually with continual stirring to a solution of 21·0 g. of  $\alpha$ -naphthyl amine in 200 c.c. alcohol. The brownish-red, but superficially greenish shimmering product of reaction is stirred with 200 c.c. of water, sucked off after standing some time with repeated stirring, and dried on a porous tile. Yield nearly quantitative.

The hydrochloride dissolves with difficulty in ether and petroleum ether, somewhat more readily in water, with dark red colour. On cooling the hot, deeply red alcoholic solution, it precipitates in the form of doubly refractive small prisms or little stars with a green surface lustre.

The hydrochloride is shaken at room temperature half an hour with 300 c.c. of cold N sodium carbonate solution. The free brown amine is sucked off, shaken twice more with 200 c.c. of sodium carbonate solution, and washed with distilled water until the filtrate is free from chlorine acid carbonate. On heating with water it changes gradually into a small crystalline, red form. Sometimes this rearrangement occurs quite by itself, if one leaves the moist product for some days. In concentrated sulphuric acid the amine dissolves, giving a reddishviolet solution. Diluted with water it separates as a reddish-brown, flocculent precipitate. It is difficultly soluble in ether and petroleum ether, giving a yellow solution, readily soluble in alcohol, benzene, chloroform and acetone, giving red to brown-red solutions. It dissolves very easily in nitrobenzene and pyridine. For recrystallization alcohol is suitable: shining, apparently monoclinic dark-red crystals. It melts at 156° to an amorphous lacquer, strongly inclined to super-cooling. On heating it changes into the crystalline solid state; not crystalline-liquid.

p-N-dimethylamino-benzal-I-aminonaphthalene-4-azobenzoicethel Ester.—The mixture of a hot solution of I·6 g. of I-aminonaphthalene-4-azo-benzoic-ethyl ester in 50 c.c. of alcohol and a solution of 2·0 g. of dimethyl amino benzaldehyde in IO c.c. of alcohol is boiled for one hour. After one hour shining crystals start to separate. Their quantity increases on cooling. Yield 0·4 to I·7 g., sometimes nothing; I cannot say why. The condensation product dissolves in concentrated sulphuric acid to a blue-violet solution; it is only slightly soluble in petroleum ether, somewhat more in alcohol, acetone and ether, very readily soluble in chloroform and benzene. For recrystallization acetone is most suitable.

The red, extended, strongly pleochroitic prisms melt at 188-189° crystalline liquid and at 197° amorphous liquid. Slowly cooled at first, the crystalline liquid, then the crystalline solid, state is reached. By rapid cooling in ice of the amorphous or the crystalline-liquid melt, the crystalline-liquid melt can be kept super-cooled. It has, at room temperature, all the properties of a nearly clear glass, is hard and brittle, can be scratched and split by a needle, does not stick. Its stability is diminished after two to three days. At the third day it has, for the greater part, become crystalline solid.

Between cover glasses the crystalline-liquid melt is oriented uniformally uniaxial. In the conoscope the optically positive uniaxial interference diagram goes over during the cooling into the biaxial one (distorted uniaxial). By rapid cooling the uniaxially-arranged film may be super-cooled. In addition to layers, which are still uniaxially oriented and by transmitted light seem to be light yellow, there are others of orange-red colour, giving biaxial positive interference. The limits between the two forms are sometimes sharp but sometimes ragged. The super-cooled liquo-crystalline glass set completely crystalline-solid between two glass plates after nearly five days. On slow cooling the melt solidified between 125 and 130° to spherolites; a second phase was observed.

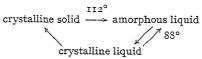
$$\text{C}_{28}\text{H}_{26}\text{N}_4\text{O}_2:$$
 Calc. N, 12·4; Found N, 12·4.

The object, to prepare liquid-crystalline resins, lacquers and glasses, which are stable for a long time at room temperatures, was completely reached. An X-ray investigation of the dimethylamino ester, specially at low temperatures, was most desirable.

Based on these experiences I succeeded in discovering a most remarkable pleochroitic circular crystalline-liquid substance, which as a chemical compound was described many decades ago, but whose crystalline-liquid properties have remained unknown. By decomposition of commercial pulegon 5 with formic acid one obtains active I-methyl-cyclohexanon-(3) and by condensation of this product with two molecules of anisaldehyde in methyl-alcoholic alkaline solution and standing for 5 to 10 days at room temperature there is obtained:—6

Active Dianisal-l-methyl-cyclohexanon-(3).—The decrease of the crystallinity is obtained here by the lateral methyl group and by the hydrogenated benzene ring. If we take instead of the anisole residue the p-ethoxyl benzene residue, which has a stronger liquid crystalline effect, or if one substitutes the methylcyclo-hexanone by the active methyl cyclo-pentanone, we lose the effect of the formation of liquid-crystalline, pleochroitic, circular resins, stable in the super-cooled state.

The l-methyl-cyclo hexanon-(3) investigated (B.P. 167-169° at 760 mm.) had the optical rotation  $[\alpha]_D^{21} = +$  13.0°. The dianisal compound recrystallized from methyl alcohol shows prismatic tabular forms of growth and melts at 112° amorphous liquid; monotropic crystalline liquid. On cooling of the amorphous melt the crystalline-liquid phase appears at 84° and this melts with rise in temperature to 88°, amorphous liquid.

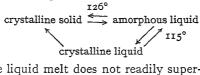


The crystalline-liquid melt can readily be super-cooled down to room temperature to form a readily coagulable resinous liquid-crystalline mass. Inoculated with solid crystals, or heated, it hardens gradually crystalline solid. Under a cover glass, by touching it with the needle, the milky and turbid crystalline liquid is oriented uniaxially and cleared, but this crystalline-liquid uniaxial layer (in the same way as many other optically active crystalline liquid melts) does not become so completely clear, as inactive uniaxial crystalline-liquid layers. The crystalline liquid uniaxial melt of dianisal-methyl-cyclohexanone, stable for two to

Wallach, Liebigs Ann., 289, 338, 1887; Klages, Ber., 32, 2567, 1899.
 Wallach, Chem. Zentr., 1, 639, 1908; Mallison, Diss., Gottingen, 1908;
 Huth, Diss., Halle, 1909; Vorländer, Ber., 54, 2261, 1921; 58, 134, 1925.

three days, is very weakly pleochromatic at room temperature, and does not reach the high optical rotation of other more pleochroitic crystalline liquids, but has, nevertheless, when investigated under the conoscope, optically negative character of double refraction, thus following the general rule. Layers, 0.02 mm. thick, of the crystalline-liquid phase of dianisal-ketone between amorphous quartz plates at 18-20° exhibit a rotation of  $-2.6^{\circ}$  (for 1 mm.,  $-130^{\circ}$ ); in benzene solution (conc. 6.40) at 19° [ $\alpha$ ]\_D^19 =  $-53.4^{\circ}$ ; in this case the melt and the solution have the same sense of rotation.

The active Bis-ethoxy-benzal-1-methyl-cyclohexanone-(3) also is a monotropic crystalline liquid.



but the crystalline liquid melt does not readily super-cool to room temperature.

Amongst the cholesterin compounds **cholesteryl bromide** <sup>7</sup> in particular forms a pleocircular melt which is quite stable at room temperature, which can easily be uniaxially oriented mechanically. Since the publication of my paper in the year 1931 our views upon the geometrical chemical structure of cholesterin have changed in consequence of the investigations of Diels, Windaus, Wieland and others. These views correspond better than hitherto with my theory on the linear crystalline effect of the molecules. Corresponding with the plane hydrocarbocyclic nature of the cholesterin molecules, there is a tendency to form super-cooled, amorphous and feebly crystalline melts.

<sup>7</sup> J. Fischer, Z. physik. Chem., 160A, 110, 1932.

#### IV. CYCLO-PENTANONE AND CYCLO-HEXANONE.

By D. Vorländer (Halle-a-S.).

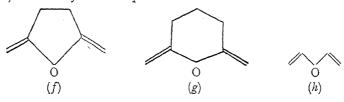
Received in German on 18th January, 1933, and translated by Dr. E. Friedmann.

Both of these ring-ketones can be condensed with two molecules of para-substituted aromatic aldehydes to form crystalline liquid  $\alpha$ -unsaturated ketones, e.g., dianisal-cyclo-pentanone,

$$CH_3O \cdot C_6H_4 \cdot CH : C_5H_4O : CH \cdot C_6H_4 \cdot OCH_3$$

(Fig. f and g), whilst the corresponding not ring-shaped  $\alpha$ -unsaturated ketones from acetone, e.g., dianisal acetone

$${\rm CH_3O}$$
 .  ${\rm C_6H_4}$  .  ${\rm CH}$  :  ${\rm CH}$  .  ${\rm CO}$  .  ${\rm CH}$  :  ${\rm CH}$  .  ${\rm C_6H_4}$  .  ${\rm OCH_3}$  (Fig.  $h$ ) are not crystalline liquid.



In the figures the keto-group is indicated by O, the aldehyde group by double lines.

On account of its uneven and not parallel ended zigzag line we recognize in system (h) the absence of linear structure and the deficiency of stable direction. In the ring ketones (f) and (g) a greater stability of direction is to be supposed, but on the whole the linear structure is missing, just as in the system (h) containing an open chain. The two double lines form one with another an obtuse angle.

An exact investigation demonstrated that the somewhat weak crystalline liquid manifestations appear in the angular ring systems only when the side chains, indicated by double lines, have of themselves a sufficiently linear structure; the aldehydes must be long, aromatic, preferably para-substituted, in order to make the diarylidene-ring ketones crystalline fluid; the rings then give to the whole molecule the necessary stability of direction, which is missing in the open-chain molecule from acetone.

I obtained the same results with *ortho-* and *meta-*substituted benzene derivatives, where, in spite of the acute-angled and obtuse-angled configuration of the whole molecules we get crystalline liquid derivatives, as soon as the two side chains are sufficiently long stretched, as shown schematically by Fig. (i):—



In these angular structures the liquid-crystalline order cannot result in such manner that the molecules will associate in the direction of the long legs, but only so that the molecules are superimposed on one another with their planes and their stretched side chains forming parallel bundles. The influence of the angular configuration as a whole is demonstrated by the relative weakness of the crystallinity, in the tendency to amorphism and in the formation of super-cooled amorphous or crystalline-liquid fusions. On the other hand, in the isomeric linear para-derivatives (k) an immense increase of crystallinity is obtained, to such an extent as to give supra-crystalline liquid or supra-crystalline solid forms, which give practically no amorphous fusions, or none at all. New liquid-crystalline forms are not produced by these systems, nor is the number of the liquid-crystalline phases, the polymorphism in crystalline-liquid state, raised, as the sides are materially of the same kind.

The bis-arylidene ring ketones from cyclopentanone and cyclohexanone exhibit but few differences: In the previous paper it was emphasized that the methylated cyclopentanone derivatives are somewhat more crystalline fluid than the methylated cyclohexanone derivatives; geometrically the obtuse angle in the pentagon gives a somewhat closer approximation to a straight line than in the hexagon. Now it is known, from the tetrahedral configuration of the carbon atoms in cycloparaffins, that the carbon atoms in cyclopentane can be arranged in one plane without strain, an arrangement which is not possible in the case of cyclohexane. The models of molecular structure (not reproduced here), of the two bis-arylidene ring ketones show distinctly, that in cyclopentanones the double lines of the two side chains are in one plane, but

<sup>&</sup>lt;sup>1</sup> Ber., **62**, 2831, 1929; **65**, 1101, 1932.

in cyclohexanones, in different planes. This difference affords a ready explanation of the stronger crystalline-liquid properties of the methylated bis-arylidene cyclopentanone.

In quite another fashion, the great stability of the direction of movement in cyclopentanone as compared with cyclohexanone can be deduced. I measured with Josef Fischer the mechanical double refraction of the two liquid ketones in the cylinder apparatus of Maxwell-Kundt, which was modified by me last year to make it possible to measure easily movable oils.2

In the following table D means the double refraction measured in  $m\mu$  along the length l per dm. of the layer, u the number of revolutions per second, z the viscosity (water = I) at the temperature t; M the molecular weight. The specific double rotation 3

$$[D] = \frac{100 \, D}{u \cdot z \cdot l}$$

can be brought into relation with the directional stability of the moving molecules. Both ring ketones exhibit a positive double refraction; so the pentagons and hexagons move mainly in the direction of their diagonals.

t = 17	LOPENTANONE $Z_{17} = I \cdot 0$		Cyclohexanone. $t = 17^{\circ}$ ; $Z_{17} = 2.3770$ .		
u/sec.	D.	[D].	u/sec.	D.	[D].
6·5 7·0 9·0 9·5 13·0 16·25 22·0	0·390 0·370 0·510 0·514 0·730 0·726 0·887 1·240	5·47 4·85 5·21 4·94 5·10 5·10 4·98 5·15	7·5 7·5 11·0 13·5 15·0 18·5 26·0 30·0 30·0	0·426 0·390 0·550 0·727 0·763 1·10 1·40 1·58 1·61	2·39 2·19 2·10 2·27 2·14 2·50 2·26 2·21 2·26

The [D] values indicate that the directional stability of movement is more than twice as great in cyclopentanone as in cyclohexanone. In the same cylinder apparatus at equal mechanical charge acetone shows no double refraction whatever. The connection between molecular stability of the direction of movement and liquid-crystalline properties seems to be established in this case with great probability.

Ber., 65, 1756, 1932.
 Vorländer, R. Walter, Z. physik. Chem., 118, 1, 1925.

# V. THE POLYMORPHISM OF LIQUID CRYSTALS. A—DEMONSTRATION.

By D. VORLÄNDER (Halle-a-S.).

Manuscript in German received 21st February, 1933, and translated by F. I. G. RAWLINS.

It has been maintained on the basis of X-ray investigations that only two types of liquid crystals exist, and, further, that no more varieties are possible. In contradistinction to this, I have found substances with three and four liquid-crystalline phases. In polarized light, with a microscope projector, it is possible to exhibit the following series of compounds:—

Monomorphous liquid crystal: p-azoxyphenetol,

amorphous liquid \$\leq \liquid \text{crystal} \leq \text{solid crystal.}

Dimorphous liquid crystal: phenetol-azoxybenzoic acid allyl ester,

amorphous liquid ≤ liq. cryst. I. ≤ liq. cryst. II. ≤ solid crystal. Trimorphous liquid crystal: p-phenetolazoxybenzoic acid phenyl ester, amorphous liquid ≤ liq. cryst. I. ≥ liq. cryst. II. ← solid crystal (I. and II)

liq. cryst. III.

Tetramorphous liquid crystal: Terephthal-bis-p-amino-cinnamic acid ethyl ester,

amorphous liquid ≒ liq. cryst. I. ≒ liq. cryst. II. ≒ liq. cryst III. ≒ liq. cryst IV. ≒ solid crystal.

My anisal-p-amino-cinnamic acid ethyl ester (by virtue of which it has been denied that there is a third liquid-crystal phase) forms two solid crystalline species. On heating the first only two liquid-crystalline forms appear, whereas the second yields three without any doubt. On cooling the liquid-crystalline phase I. with reference to the amorphous melts, three liquid-crystalline phases always become visible:

amorphous liquid  $\stackrel{139^{\circ}}{\leftrightarrows}$  liq. cryst. I.  $\stackrel{118^{\circ}}{\leftrightarrows}$  liq. cryst. II.  $\stackrel{83^{\circ}}{\leftrightarrows}$  solid cryst. I.  $\stackrel{108^{\circ}}{\leadsto}$  solid cryst. II.

The anisal ester is a substantially uniform and pure material (*Trans* form). Numerous fractional recrystallizations from alcohol have so far failed to yield any appreciate quantity of isomeric esters. The separate transitions, which are sharper the purer the ester, become apparent through the discontinuous changes in the tenacity of the liquids, as well as by thermal effects. The slowly-growing spherulithic solid crystal form I., on unsuitable super-cooling, changes over to the liquid crystal form III., so that the latter passes over immediately into the solid crystalline form II. as indicated by the arrows. The solid crystals of

anisal ester obtained from alcoholic solution at room temperature are small plates showing straight extinction, and are usually identical with solid crystals II. On heating these crystals in a small tube or under the microscope one observes only the transitions 108° ( $\rightarrow$  liquid-cryst. II.), 118° ( $\rightarrow$  liquid-cryst. I.), and 139° (amorphous liquid).

118° ( $\rightarrow$  liquid-cryst. I.), and 139° (amorphous liquid).

The viscous liquid phases of p-phenylbenzal- and terephthalamino-cinnamic acid ethyl ester (liquid-cryst. IV.) have been confirmed by X-ray photographs by K. Herrmann and A. H. Krummacher: thus we are not concerned here with soft solid crystals, but rather, liquid crystals.

The existence of polymorphic liquid crystals yields peculiar information on the derivation of substances. For instance, it is possible to derive phenetol azoxybenzoic ethyl ester from the two esters, p-azoxyphenetol with its oily liquid-crystalline phase, and p-azobenzoic ethyl ester with its rod-shaped liquid-crystalline phase of a different kind. If we combine these two forms, small rods and slimy oil, into one complex, namely into phenetolazoxybenzoic ethyl ester, we obtain two isomeric hybrids, one of which occurs as a dimorphous liquid crystal (slimy oil and small rods), and the other in one form only as slimy oil:—

liquid crystal monomorphous: slimy oil.

The hybrids (1) and (2) cannot be coupled further.

It was to be expected that investigations into the polymorphism of liquid crystals might furnish not only important data concerning the nature of molecules, but also might further our still imperfect theoretical knowledge of the arrangement and parallel orientation of the rod-like molecules in liquid crystals. The supposition that one and the same substance cannot exist in more than two liquid-crystalline forms is undoubtedly erroneous.

# A SIMPLE ARRANGEMENT TO DEMONSTRATE LIQUID CRYSTALS.

By G. VAN ITERSON, JR. (Delft, Holland).

Received 10th March, 1933.

O. Lehmann's remarkable observations with regard to crystallisation phenomena were doubtless due to the fact that he had at his disposal apparatus by means of which he could study his microscopic objects at high temperatures which could be regulated in a very exact manner. This exact regulation was possible because he was able to heat his objects as well as cool them. He proceeded in such a way that the temperature was first raised to a rather high degree without special precautions, and then slowly and carefully lowered with the cooling arrangement. Observation of the microscopic object at the same time allowed Lehmann to notice when special phenomena occurred, after which he was able to vary the temperature between very narrow limits around the "transformation temperature" by changing the speed of the cooling arrangement. It goes without saying that a rough initial regulation of the temperature with the heating arrangement was applied.

In the beginning (for the first time in 1877), O. Lehmann obtained heat by means of a small burner, which could be turned under the stage and in this manner could heat the slide through the opening in the stage. Obviously the condenser had to be eliminated, and the application of a polariser required special provisions. This special arrangement has been applied also by Lehmann to many other varieties of his "crystallisation microscope." To this category belong also the most usual types of this microscope, namely those which Steeg and Reuter in Homburg a.d.H. and C. Zeiss (construction by Prof. H. Siedentopf)

supply to the trade.2

The advantage of the Zeiss' crystallisation microscope lies in the fact that it may be constructed from a common Zeiss microscope and a number of accessory parts.

For accurate determinations, O. Lehmann used a method of heating by means of an oil bath, while in later years he applied also electric heating arrangements, as to which, however, he remarked in his latest publication that they are not as successful in general as heating with a small gas-burner under the stage.

To effect cooling, O. Lehmann used a current of air, which was conducted above the slide by means of a small tube by the side of the objective; sometimes two of these small tubes were used. A small pair of bellows was used to produce the air current.<sup>3</sup> Especially important

<sup>1</sup> Vide O. Lehmann, Das kristallisations Mikroskop u.s.w., Braunschweig, 1910.

<sup>&</sup>lt;sup>2</sup> A description of these apparatus are to be found in Lehmann's last publication, published six years after his death: "Methoden zur Darstellung and Untersuchung flüssiger Kristalle," in *Handb. der biol. Arbeitsmethoden*, III., AI, 132-352, 1928.

<sup>&</sup>lt;sup>3</sup> This pair of bellows may be found in O. Lehmann, *Molekularphysik*, I. Bd., 125, 1888. We have successfully used a small pump of the type of the bicycle tyre pump instead of it. Such a pump is less perishable.

was the fact that the air current could be more or less directed by means of the little tube; in this way a "region of transition" of the temperature was produced in the middle of the field of vision, where changes of state of the matter were occurring.

Other investigators, studying the crystallisation phenomena at elevated temperatures, have used similar arrangements. D. Vorländer <sup>4</sup> advises, in addition to the use of the above-mentioned crystal-microscopes of Steeg and Reuter and of Zeiss, the application of a small gas burner under the stage of a common laboratory microscope, or the use of an electrically heated microscope stage. Vorländer does not mention a cooling arrangement in the latter cases, by the omission of which, im-

portant advantages of Lehmann's arrangement are lost.

In point of fact, everybody who has worked with Lehmann's arrangement will have observed that a larger field of observation with the microscope has been obtained, which has become indispensable. For instance, the crystallographer R. Brauns observed in the introduction of his publication Flüssige Kristalle und Lebewesen, 170 Referate, Stuttgart, 1931: "Bei meinem Wechsel der Universitäten Giessen-Kiel-Bonn gehörte ein Lehmann'sches Kristallisationsmikroskop immer zu den ersten Anschaffungen." Unfortunately, such a microscope belongs still to the category of rare laboratory equipment. D. Vorländer mentioned, as far back as 1907: "Bei jeder, auch noch so geringsfühigen Anomalie beim Schmelzen und Erstarren kann sich dann an die Vorprobe die genauere Untersuchung mit Objektträgern, Deckgläschen and mit dem heizbaren Polarisationsmikroskop anschliessen, dessen Gebrauch zwar vor mehr als 15 Jahren von O. Lehmann empfohlen wurde, dem Chemiker aber fremd blieb." This statement may still be applied to present conditions.

Doubtless the slight familiarity with Lehmann's crystallisation-microscopes is due to their high costs of purchase; this applies also to the accessory parts of Zeiss. Moreover, Reuter and Steeg's microscope does not lend itself easily to other purposes. To "rebuild" a microscope into a crystallisation microscope is now relatively easy, but not everybody has an instrument available for this purpose. Moreover, a microscopist will be somewhat afraid, as a rule, to put a gas flame under

his stage.

There will be found below the description of a simple and not expensive arrangement to be used instead of the crystallisation-microscope. This arrangement has been introduced by the writer in the laboratory of Technical Botany of the Technical University of Delft. Quite often more than twenty-five students have these appliances simultaneously at their disposal, which proves that the apparatus can be used for laboratory exercises—which cannot be said about the above-mentioned apparatus available in the trade.

The principle on which the new arrangement is based follows that of O. Lehmann's crystallisation microscope. The slide is warmed up to a degree slightly higher than required, after which it is cooled off to the desired temperature by means of a current of air, during which period observations are made with the microscope. The temperature at which a transformation to liquid crystals occurs can be maintained for an unlimited time.

The apparatus is shown in Figs. I and 2, Fig. I giving a general view, while Fig. 2 contains a cross-section and four projections. In the

<sup>&</sup>lt;sup>4</sup> Chemische Kristallographie der Flüssigheiten, p. 49, Leipzig, 1924. (The cover of this little book shows illustrations of both these crystal microscopes.)

first drawing a slide is shown in its position in the apparatus. That part of the apparatus which resembles a "box" open on one side is placed on the right-hand side of and next to the microscope. The rectangular tube which projects from the box on one side is placed above the stage, but

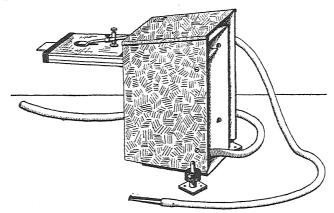


Fig. 1.—Apparatus to demonstrate liquid crystals, general view.

does not touch the latter; the objective, moreover, has no contact with the rectangular tube. Microscope and apparatus do not touch one another in any way. The microscope is to be placed in such a way that the axis of the microscope tube passes exactly through the centre of the openings in the top and bottom of the rectangular tube.

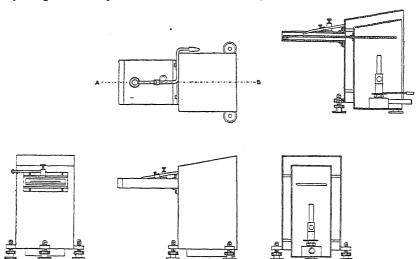


Fig. 2.—Apparatus to demonstrate liquid crystals, cross-section and projections.

The microscopic object to be studied is prepared on a slide of English size (3 by I inches) and placed about three-quarters of the way along the length of the slide, starting on the left. The slide is pushed into the rectangular tube, where it rests on a copper plate, which continues into the box. Care is needed that the microscopic object lies exactly on the

opening in the copper plate, which opening corresponds with those in the rectangular tube. The slide is moved by means of its projecting end, allowing in this manner adjustment to a position suitable for observation.

The copper plate in the box is heated by means of a small type bunsen burner, of which the gas and air feeds may be regulated,<sup>5</sup> which heating transmits by conduction into the part of the copper plate within the rectangular tube. The size of the flame and the position where the burner is placed will have to be adjusted according to the nature of the object to be studied. In every case this has first to be tried out.

It will be apparent that the rectangular tube serves to avoid heating of the stage and the objective as much as possible. To this purpose, it has been made from slate (we use pieces taken from ordinary school slates); nevertheless, care is to be taken that it does not come into contact with the stage. Therefore, three adjusting screws have been fixed to the apparatus. It is sufficient to produce a free space of I millimeter between the stage and the rectangular tube; to effect good lighting by means of the condenser of the microscope it is advisable not to make this free space larger. Meantime it has become apparent that the adjusting screws allow only a restricted magnitude of regulation, and since the heights of the stages of various microscopes vary to some extent, it will be necessary to take the height of the stage into account to some extent when constructing the apparatus. The box is double walled, avoiding heating of the microscope to any extent, even if the copper plate is heated to a relatively high degree; the observer himself does not experience any trouble.

Cooling of the slide is done by means of an air current which is conducted to it by a little tube attached to the top of the rectangular tube, and which leads to a point next to the objective by means of a groove on top of the rectangular tube. The little tube is adjustable in a vertical direction by means of an adjusting screw. Furthermore, a mouthpiece is attached which is movable; mouthpieces of different shapes may be This arrangement allows a careful regulation of the position of the little tube, which is of importance if the air current is to be led to the desired spot on the slide. The air current is produced by blowing with the mouth. To this end there is connected to the metal tube a piece of rubber tubing, in which a mouthpiece is inserted. We prefer a mouthpiece of hard rubber, taken from a cigar holder. While observations are being made, this mouthpiece is kept between the teeth. In this manner a very simple method of cooling is obtained; moreover, it appeared to me that the air current is more exactly regulated by the mouth than with a small pair of bellows. This method also leaves both hands free.

The advantages of the new apparatus may be summarised as follows:

- I. The apparatus may be used with every type of microscope, without making any changes in the latter.
- 2. The same apparatus may serve with very different types of microscopes; the only change at the most being the alteration of the lengths of the legs, which may easily be overcome by using a little wooden board under the apparatus or under the microscope.
- 3. The polarising attachment belonging to the microscope may be used without alterations.
- 4. The apparatus is completely independent of the microscope, heating is produced with a burner in the box, next to the microscope, the stage and the objectives are only slightly heated.

<sup>&</sup>lt;sup>5</sup> We obtained these burners from G. Köchert, Ilmenau.

5. The apparatus may be built up from easily obtainable materials, and is not subject to deterioration except for two pieces of rubber tubing.

6. At a low cost it is easily made by an instrument maker of normal

ability in a laboratory workshop.

With this arrangement, several experiments as described by O. Lehmann 6 may be made, as well as several of those communicated by D. Vorländer or by G. and E. Friedel. 7 We mention specially in this respect his experiments on liquid crystalline matter, which one encloses in "glass-capillaries."

However, we do not wish to conceal the fact that some experiments proved troublesome. For instance: "conoscopic observation" is difficult when using this apparatus, because high magnification is preferably avoided, and also because the condenser is rather far away from the object.

At any rate, by describing this new apparatus, I hope to have succeeded in bringing the possibility of observing the phenomena of matter in paracrystalline state within the reach of a larger number of people than there are at present. Naturally I have in mind biologists in the first place. Reinitzer, who observed the deviating behaviour of cholesterin benzoate at the melting-point, and who sent this material to O. Lehmann (this was the first time that distinctly liquid crystals were observed), was a botanical physiologist. Other biologists also occasionally mentioned liquid crystalline matter. But the significance of the liquid crystalline state in explaining the phenomena in living cells is practically exclusively demonstrated by crystallographers. This is true, for instance, for F. Rinne, who stressed this in his publications, Spermien als lebende flüssige Kristalle (Naturwiss., 18, 837-841, 1930), and in his nice little booklet, Grenzfragen des Lebens, Leipzig, 1931. Most "biologists" are unfamiliar with the phenomena in question, because they lacked the tools with which to observe them.

<sup>6</sup> In addition to the publications cited above (we refer specially to the series of experiments in *Das Kristallisier mikroshop*) we mention: *Die neue Welt der flüssigen Kristalle*, Leipzig, 1911, and *Flüssige Kristalle and ihr scheinbares Leben*, Teinzig 1921.

Leipzig, 1921.

7 Les propriétés physiques des stases mosomorphes en général et leur import-

ance comme principe de classification, Z. Kryst., 79, 1-61, 1931.

# FORCES CAUSING THE ORIENTATION OF AN ANISOTROPIC LIQUID.

By V. Fréedericksz and V. Zolina.

Received 18th April, 1933.

The investigation of the forces tending to orient an anisotropic liquid is possible in many ways. The existence of an anisotropic state, as differentiated from an isotropic state, requires the presence of a special force acting between the molecules or between groups of molecules. These forces exhibit the property, over a given temperature range, of giving the molecules a definite orientation without altering its property of mobility as a liquid. The hypothesis of swarms may be interpreted as follows: There are two stages in the orientation of molecules in

liquid crystals. The first state is the formation of molecule-groups or swarms which can in no case be considered as parts of a solid body. Apparently they may vary widely in external form and outline. With respect to the number of molecules composing them they may vary not only from one group to another but from time to time. The orientation of the molecules in a swarm constitutes the distinguishing feature of the latter.

The different swarms also interact upon one another, constituting the second stage in the orientation of an anisotropic liquid. Temperature effect, in the absence of external influences, is sufficient to prevent the mutual orientation of swarms with respect to one another. External influences (due to the walls of a vessel, electric or magnetic fields) are often present to a degree sufficient to eliminate in a certain measure the effect of temperature. In thin layers or in magnetic fields, sheets of anisotropic liquid are often observed in no way differing in many respects from sheets of solid crystals.

The hypothesis of swarms may also be interpreted somewhat differently. Let us take into consideration all the forces acting on a molecule, not only those of neighbouring molecules, but also the external forces (such as those of an electric or magnetic field). Under these conditions the temperature effect at a given temperature restricts the molecular groups to a definite volume. The group of oriented molecules contained in this volume, and of which the orientation is not disturbed by the temperature effect, constitutes a swarm. The boundary of a swarm may be considered as the boundary of a sphere of action whose radius depends upon the molecular and external forces taken together, as well as upon temperature. Within such a sphere of action there takes place a certain molecular orientation which is no more affected by the temperature that than of a solid body. In view of this, the question of interaction between swarms does not come into question. The orientation of molecules inside a swarm will differ with differing external conditions. For instance, a thin sheet of an anisotropic liquid held between two glass plates comprises a single swarm. The lines of double refraction observed in such layers indicate a change of orientation of the molecules within a single swarm, the volume of which is equal to the entire volume of the liquid. On the other hand, in the case of the experiments of W. Kast, M. Jezewski, and K. Hermann and A. H. Krummacher, we have swarms whose volumes comprise a very small portion of the total volume.

The calculation made by Ornstein in his paper "Experimentelle und theoretische Begründung der Schwarmbildung in flüsszigen Kristallen." 2 corresponds to the first of the above views. The method which he employs may be used, if not always, at least in some cases, in the calculation of the orientation of molecules within a swarm. However, this problem has, unfortunately, not been sufficiently treated from the mathematical standpoint, and it is very difficult to make any definite conclusions from experimental work done on this subject.

Among the methods which may be applied to the investigation of the interacting forces between molecules or swarms may be mentioned the spectroscopic method, and those utilising electric and magnetic fields. The preliminary results of some experiments now in progress may be of assistance in the solution of this problem. 1. In one of the earlier papers 3 it has already been shown that the critical boundary determined by the action of a magnetic field on a

plano-concave homogeneous sheet is independent of the kind of glass used. This investigation was continued and at the present time it may be stated that the critical boundary is not altered by the substitution of quartz or platinised glass, as demonstrated by the experiments of V. Zolina.

In Figs. I and 2 are given the results of the measurements of the critical thickness for two substances, para-azoxyphenetol and anisaldazin. These measurements were carried out in close accordance with those indicated in the above mentioned paper.

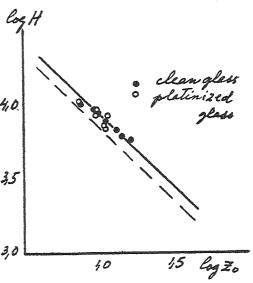


Fig. 1.-p-azoxy-phenetol.

Both substances were investigated by a magnetic field, first between clean glass surfaces and then between the same glass surfaces after

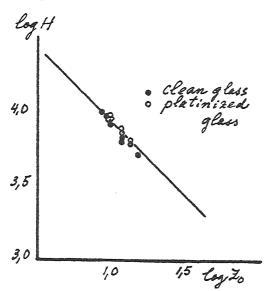


Fig. 2.—Anisaldazin.

platinisation. thickness of the platinum layer may be taken as  $2 \times 10^{-5}$  cm. On the diagram the measurements tained with platinum and without platinum are indicated by stars and circles respectively. As ordinates magnetic field strength in gauss is laid out logarithmically while as the abscissa is taken the logarithm of the critical thickness in thousandths of a millimeter.

For p-azoxyphenetol (Fig. 1) for clean glass as well as platinised glass we have

one and the same constant  $K = z_0 H = 8.40$  (c.g.s. units), in good

<sup>&</sup>lt;sup>3</sup> V. Fréedericksz and V. Zolina, Trans. Americ. Electrochem. Soc., 85, 1929.

agreement with the earlier determined values; temperature of the experiment 150° C.

For anisaldazin (Fig. 2) the results of new observations gave the same value in both cases, the constant somewhat differing from that of earlier experiments. By the new measurements K=8.4 (c.g.s. units) while at the same temperature the earlier value obtained was 7.0. This difference may be attributed to the difference in substances treated.

On the basis of these and older experiments it seems probable that the orientation of the liquid is determined (I) by the orientation of the molecules or swarms in contact with the glass, and (2) by the interaction between the molecules or swarms within the liquid. In order to demonstrate this more clearly we have developed the method explained in the following paragraphs.

2. The observations described in this paragraph are those of V. Zvetkoff (Physical Institute, University of Leningrad). Let AB be

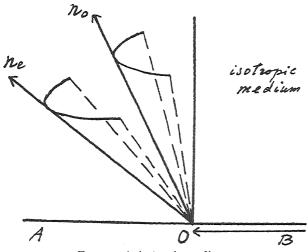
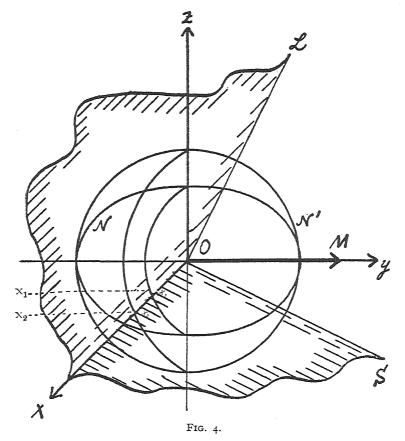


Fig. 3.—Anisotropic medium.

the surface of an anisotropic liquid (Fig. 3). If the external portion of the isotropic medium has index of refraction greater than the ordinary and extraordinary rays the anisotropic medium, then by passing the rays along the surface of the medium we obtain in the isotropic medium two cones

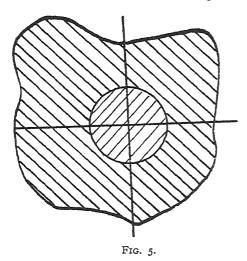
of total refraction limited by the rays  $n_e$  and  $n_o$ . In the region  $n_e$ , O,  $n_o$  we have only extraordinary rays, the plane of polarisation of which depends upon the optical axis of the crystal. In Fig. 4 let the direction of the optical axis be designated by OM, which will also be the direction of the molecules. Let the wave surface NON' of a positive crystal have its centre located at O. If XOL is the plane of incidence of rays perpendicular to the plane dividing the two mediums SOX, and if OX is the direction of the rays in the anisotropic liquid, then the limits of total internal reflections are determined by the lengths OX<sub>1</sub> and OX<sub>2</sub>. The position of the plane of polarisation within an anisotropic liquid for an extraordinary ray is determined by the plane OXM. Knowing the polarisation of the rays in the upper isotropic medium, it is possible to calculate the polarisation inside an anisotropic liquid and in this way determine the inclination OM to the surface of division, OS. If OM rotates in the plane of the drawing, SOL, or plane XOL rotates about the axis XO, then the boundary of total internal reflection does not change its position but the angle of polarisation changes between the limits O and  $\pi/2$ . The boundary of the region of total refraction may also be determined by the use of reflected rays. In this case, generally speaking, the reflected rays will be only partially polarised, but their polarisation will be sufficient to determine, by the use of an analyser, the position of the optical axis or of the molecules in the crystal. The method has the advantage that it permits one to deduce with greater accuracy the thickness of the layer adjacent to the glass which determines the plane of polarisation. In fact, we may estimate that in an angle of incidence differing from the angle of total refraction by 2° or 3°,



already at a depth of  $2 \times 10^{-5}$  cm. the energy of the green lines of Hg comprise only  $10^{-4}$  of the portion of the energy incident upon the surface itself. Since the angle between the limits of the cone  $n_e$  and  $n_e$  is of the order of  $10^\circ$  to  $30^\circ$  we are able to observe the surface utilising only extraordinary rays. If we observe para-asaxyanisol between a plane and a convex glass surface placed in a magnetic field, as was done in the experiments of A. Repiewa, V. Zolina and V. Fréedericksz, then the critical boundary between the oriented and non-oriented liquid is observed. If the observed substance had been

<sup>&</sup>lt;sup>4</sup> V. Fréedericksz and A. Repiewa, Z. Physik, 42, 532, 1927; V. Fréedericksz and V. Zolina, Z. Kristallographie, 70.

well prepared so that the axes of the molecules were not only parallel to the surface of the glass but parallel to each other, then the two regions would have been mutually perpendicularly polarised (Fig. 5). The boundary between the two regions is quite sharp and only in a very narrow circumferential region have we an intermediary state where the molecules or swarms are only partially oriented. If the substance had been less carefully prepared then this intermediary region would have proved to be much broader and might possibly have spread over the entire medium. At any rate this boundary is always distinguishable. However, the exact determination of this boundary has as yet not been accomplished but it coincides approximately with the earlier observations made by V. Zolina. It is interesting to note that after the removal of



changed positions of the molecules or swarms is partially conserved. the experiments of V. Fréedericksz, A. Repiewa and V. Zolina carried out by a different method, the position of the critical boundary did not change upon repeated application and removal of the magnetic field, absolutely no residual deformation being observable. It is apparent then that different forces act at the surface of the substance beyond a certain distance within the substance.

the magnetic field

The inclination of the plane of polarisation does not depend upon the polarity of the field. Upon the reversal of the direction of the field the inclination of the optical axis or of the molecules takes place in the same direction. Thus we may definitely state that the orienting action of the magnetic field depends upon the diamagnetic properties of the substance.

3. Certain observations made with electric fields indicate that the orientation of the molecules in such fields is due, *inter alia*, to the anisotropic dielectric properties of these substances. From observations made with magnetic fields, the electric field may be calculated which, *ceteris paribus*, will give the same effect as the magnetic field. As a matter of fact we may write the fundamental equation due to Ornstein <sup>5</sup> determining the conduction of an anisotropic liquid in a magnetic field

$$A\frac{d^2\phi}{dx^2} = v(\mu_1 - \mu_2)H^2 \sin \phi \cos \phi.$$

For an electric field we may also write the corresponding equation

$$A\frac{d^2\phi}{dx^2} = v(\epsilon_1 - \epsilon_2)E^2 \sin \phi \cos \phi.$$

<sup>&</sup>lt;sup>5</sup> L. S. Ornstein, Z. Kristallographie, 79, 90, 1931.

In this equation  $\epsilon_1$  and  $\epsilon_2$  are the two principal dielectric constants. The action of the electric field will be equivalent to the action of a magnetic field if

 $(\mu_1 - \mu_2)H^2 = (\epsilon_1 - \epsilon_2)E^2,$ 

for which

$$E = \sqrt{\frac{\mu_1 - \mu_2}{\epsilon_1 - \epsilon_2}} H.$$

On the basis of the experiments of Foex we may assume that the value of  $\mu_1-\mu_2$  is of the order of 5  $\times$  10  $^{-7}$ . If we estimate that  $(\epsilon_1-\epsilon_2)$  is of the order of 0.5, then

$$E \sim 10^{-3} . H$$

for which, when H=1000 gauss, the equivalent electric field will be E=300 volt per cm. Very many experiments such as those of K. Hermann, Krummacher, May, Zocher, Kast, as well as those of our own carried out upon thin layers of liquid the thickness of which  $Z_o$ , were such as to permit the orientation of the molecules with fields of a few thousand gauss, corresponding to electric fields of 1000 volts or less.

The observation of very many experimenters was made upon thin platinum layers deposited on glass by the cathode spluttering process. In these experiments the electrodes were partially covered by the anisotropic liquid. The electric fields used were very non-homogeneous and differed widely from those of parallel plate condensers. As soon as the field attained 300 to 1000 volts, its action upon the substance was noted. The initial value of field E, at which a change in orientation was noted (in any case in our experiments) depended upon the layer thickness. The thinner the layer, the greater this initial value. Quantitative measurements of the relation between the electric field E and the layer thickness have as yet not been carried out.

If the orientation of the layer is perpendicular to the glass (acetoxybenzalasin, ethoxybenzal-p-amino-α-methyl-cinnamic acid ethyl ester) then the direction of the greatest dielectric constant,  $\epsilon_1$ , is perpendicular to the axis of the molecules and parallel to the glass. In a homogeneous field directed parallel to the surface of the glass an orientation of the molecules cannot take place. But in fields above platinum electrodes. directed approximately perpendicular to the glass such orientation must take place. A change in orientation at one point will bring about a change at other points. In a non-homogeneous field we have not only a rotational force but a translatory force tending to set the liquid in motion. This translatory force is proportional to the gradient of the square of the field. In an isotropic liquid it is directed either towards or away from the electrodes, depending upon whether the dielectric constant of the particles is greater or less than the dielectric constant of the medium. The lines of the field and of the ponderomotive force corresponding to the form of electrodes used (thin platinum layers on glass) intersect each other at very large angles and thus it is very probable that a movement of the liquid may occur. This, however, is possible only with a sufficient absence of homogeneity of the field. In order that the translatory forces tending to produce motion may act, a rotational moment is also necessary. In the opposite case, if the entire liquid layer is homogeneous, these translatory forces are unable to produce a relative motion of one portion of the liquid with respect to another.

In the experiments of W. Kast <sup>6</sup> the electrode dimensions were  $3 \times 6$ mm. and the distance between them 4-5 mm. The field thus in this case was probably non-homogeneous. The average applied was 650 volts per cm. which seems to have been sufficient to set the liquid in motion, similar in certain respects to that described below.

It is interesting to note that in the experiments of K. Hermann, A. H. Krummacher and K. May, in those cases where there was not an anisotropic liquid above the electrodes, the action of the electric field was observed for para-azoxyanisol, a substance which is oriented parallel to the glass and has its greatest dielectric constant perpendicular to the field.

Unfortunately these investigators did not carry out experiments upon ethoxy-benzal-p-amino-α-methyl cinnamic acid ethyl ester.

In our experiments upon placing the latter substance in a practically homogeneous field of 2000 volts no orientation of the substance was observable. If the orientation had depended upon the dipole, which in this case is parallel to the axis of the molecules, then we should have been able to detect rotation.

Plate I, Figs. 1, 2, and 3, substantiate the experimental results of H. Zocher. 8 We see ethoxy-benzal-p-amino- $\alpha$ -cinnamic acid ethyl ester in an extremely non-homogeneous field between two electrodes 0.5 mm. apart. A light band at the electrodes makes its appearance at a field strength of 400 volts per cm. Total orientation penetrating to half of the distance between the electrodes occurs with average field strengths of 1100 volts per cm., that is, at values half as great as in homogeneous fields where no orientation was observed. It is interesting to compare the above photographs with those for acetoxybenzalasin, the structural formula of which is

$$\mathrm{CH_3}$$
 .  $\mathrm{COO}$  .  $\mathrm{C_6H_4}$  .  $\mathrm{CH}$  :  $\mathrm{N}$  .  $\mathrm{N}$  :  $\mathrm{CH}$  .  $\mathrm{C_6H_4}$  .  $\mathrm{COO}$  .  $\mathrm{CH_3}$ 

indicating complete symmetry, as compared with the structural formula of the first substance:

Plate II, Figs. 1 and 2, just as the earlier observations, with acetoxybenzalazine, were made by J. Afanasiewa and A. Repiewa.

The remaining photographs and latest observations were made by V. Zolina. Plate II, Fig. 1, represents the substance between crossed nicols in absence of a field. Upon the field attaining a certain value depending upon the thickness of the substance at one of the electrodes (not of both as with the above liquid), certain figures make their appearance, having forms as in Plate II, Fig. 2. These figures grow in a direction away from the electrode in proportion to the increase of the electric field. At first they are very small in size, gradually extending with increase of field, until they occupy the entire space between the electrodes. The picture with alternating as well as direct current fields is the same. The inclination of the molecular axes have their greatest value not upon the electrode surface but at some distance from it. We are dealing here

<sup>W. Kast, Z. Physik, 71, 42, 1931.
K. Hermann, A. H. Krummacher and K. May, Z. Physik, 73, 419, 1931.</sup> 8 H. Zocker and V. Birstein, Z. physik. Chemie, 42B, 186, 1929.

PLATE I.—Ethoxy-benzal-p-amino-methyl cinnamic acid ethyl ester.



Fig. 1.—400\_v. per cm.



Fig. 2.—1000 v. per cm.



Fig. 3. [To face page 926.

### PLATE II.—Acetoxy-benzalazine.

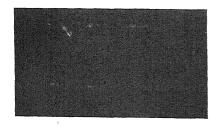


Fig. 1.

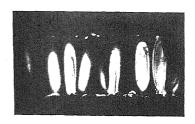


Fig. 2.

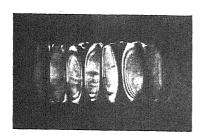


Fig. 3.



FIG. 4.

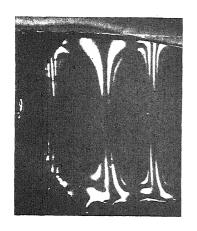


FIG. 5.

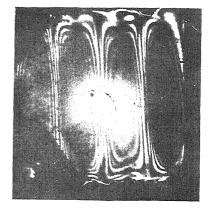


Fig. 6.

[See page 926.

### PLATE III.



Fig. 1.



Fig. 2.

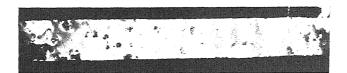


Fig. 3.



FIG. 4.



Fig. 5. [See page 927.







Fig. 5.—Homogeneous layer of anisal dazine in an arrangement according to Case III, with increasing field strength.

[See page 956.

with a very complicated case of electrostriction. No motion of the liquid is as yet observable. Upon further strengthening of the field we note developments as indicated in Plate II, Figs. 2, 3, 5 or 6. Here the interference bands are symmetrically situated with respect to the space between the electrodes. Upon observing the phenomena through a microscope of somewhat greater magnifying power it is evident that some parts of the liquid are in motion. Very fine discrete foreign particles are in motion, sometimes moving from one electrode to the other and back, sometimes in one direction only. The alternating character of the field does not in any way influence this motion. The motion does not affect the figure, so that the interference bands may be readily photographed. In Plate II, Fig. 6, the particles moved slowing along an approximately elliptical path between the electrodes. The speed of the particles in Plate III, Fig. 2, amounted to 5 × 10<sup>-3</sup> cm. per sec.

The voltage range over which stationary conditions prevail and in which the interference bands remain unchanged is very small, not exceeding 10 to 12 volts. Upon further increasing the field strength a turbulent motion of the particles sets in. When the field strength is varied in the reverse order, all the above observed phenomena are also repeated in the reverse order. When the field is suddenly removed we obtain the conditions pictured in Plate II, Fig. 4. We observe the anisotropic liquid as if in a deformed state, which persists over a period of time sufficient to photograph. All photographs were taken with the green lines of Hg.

It is to be noted that in this phenomenon the space between the electrodes is divided into equal parts. Plate II, Figs. 3, 4, and 6, were taken with a potential difference of 82 volts, Plate II, Fig. 2, with 58 volts. The action of the field was first noted at 55 volts.

Plate III, Figs. 1, 2 and 3, represent a very much less carefully oriented substance. With a distance between the electrodes equal to 0.5 mm., a stationary condition was obtained at 30 volts potential difference. Lack of proper orientation hinders, but does not prevent the formation of a stationary condition. The number of separate rectangles into which the inter-electrode space is divided depends upon the inter-electrode distance. The interference figures may vary considerably. Plate III, Fig. 4, represents a quite carefully oriented substance. The average distance between electrodes was here 0.2 mm., on one side somewhat greater than on the other. The distance between sections of similar structure was somewhat less at the narrower than at the wider end. The thickness of the layer was much less than in the preceding case and required a potential of 72 volts to produce a stationary condition of the liquid. Finally in Plate III, Fig. 5, we note another picture of interference. Here the inter-electrode distance was 0.5 mm.

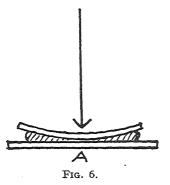
It is to be noted that, immediately upon the field attaining a value sufficient to produce a new orientation, an agitation characteristic of this moment is to be observed. The space between the electrodes, especially the space adjacent to the electrodes, appears illuminated with flashes of light of very short duration.

The above experiments were carried out only to compare the results with those of other investigators. The quantitative study of these phenomena remains to be continued. The above phenomena might be considered as some breakdown of a dielectric if an increase of current had been observed. It is very probable that K. Hermann, and A. H. Krummacher were quite correct in considering that the experiments

of W. Kast carried out with Röntgen rays may be explained by means of the motion of an anisotropic liquid. It seems to us, on the basis of our observations, that the cause of this motion is the dielectric anisotropy of the liquid and the very complicated phenomena of electro-striction occurring in it.

4. The question of the elastic deformation of an anisotropic liquid is of very great interest. In the following, a few preliminary observations are described which show a change in orientation produced by mechanical forces. Especially advantageous for this purpose was a ethoxy-benzal-para-amino- $\alpha$ -methyl-cinnamic acid ethyl ester.

The substance was placed between the convex side of a watch glass and a plane glass. The above-named substance has the advantageous property of very easily forming a layer oriented perpendicular to the glass. The observation was, as usual, carried out through a microscope and crossed nicols. If we press on the watch glass with a sharp object at A, (Fig. 6) a compression of the liquid is produced or a very small quantity

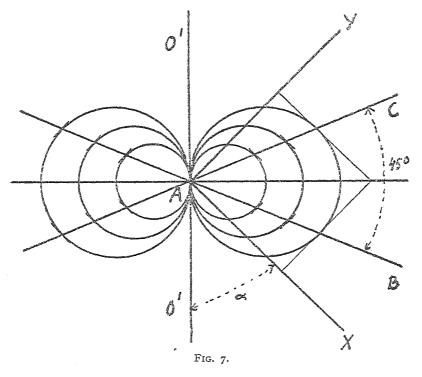


of the substance is ejected from the point A. The result of this is an apparently instantaneous re-orientation of From the normal the entire liquid. position the substance takes on an orientation nearly parallel to the surface of the plane glass. In monochromatic light a very great number of rings of equal double refraction are visible. In addition to these, four straight lines are visible intersecting in the point A, these also being visible in white light. These 8 branching radii form nearly equal angles of 45° between each other. The position of these straight lines is more or less

random, and differs from one case to the other. This picture is observed only when the watch glass is in motion. The moment the watch glass becomes again stationary the anisotropic liquid more or less rapidly returns to its former condition.

The position of the four straight lines enables one to judge of the disposition of the axes of the molecules or swarms inclined to the plane glass. If the axes of the molecules are tangential to the circles indicated in Fig. 7, the latter forming a figure "8" near the centre A of the substance, and if the directions of the crossed analyser and polariser are AX and AY, respectively, then molecules disposed along the lines AC and AB located at an angle of 45° with respect to one another, will be parallel to the analyser or the polariser, and therefore will not transmit light. There are eight such straight lines in all, the position of which depend upon the angle between the normal AO' and plane of polarisation AX. Obviously upon applying pressure upon the watch glass, the particles in the crystal portion at A assume an orientation parallel to the glass in directions varying from one case to the other. This orientation parallel to the glass indicated in Fig. 8 extends over the entire liquid. The deformation of orientation brought about by the motion of the watch glass ceases with the motion. As was pointed out by Zochert and Birstein 8 a similar orientation of molecules may be observed about definite points or lines (unstetigkeits Linien oder Punkte) which comprise one of the distinguishing characteristics of the nematic phase. In other anisotropic liquids which also give normal layers, as for instance acetoxybenzalasin, a similar phenomena was not observed.

Ethoxy-benzal-p-amino-cinnamic acid ethyl ester also presents another phenomenon which is probably related to that just described above. Under observation with the microscope, as above mentioned, owing to accidental jars given the instrument, some regions of the substance became luminous. The liquid also appeared to be in agitation, the illumination seeming to be connected with this agitation. Upon jarring the microscope more violently, this illumination persisted longer. It seems as if the liquid were in a state of oscillation. This assumption is confirmed in that the oscillations may be strongly increased and sus-



tained by means of a tuning fork pressed to the microscope. We may also bring about these oscillations by means of any other periodic, mechanical shocks, for instance, by using a small motor rotating at a sufficiently high speed. At correspondingly high frequencies sharply outlined interference figures may be observed. The sharpest figures were obtained at 200 to 300 vibrations per second. Upon vibration frequencies of the tuning fork of an octave or more higher, the oscillations gave only a somewhat sharper picture than when produced by ordinary shocks. The picture observed through the microscope is shown in Fig. 8. Two mutually perpendicular straight lines and two approximately hyperbolical curves, at sufficiently intense oscillations, stand out in white light very sharply and are very thinly outlined. Such figures are similar to the nodal lines of vibrating plates.

With weak oscillations or jars of the microscope these lines are greatly broadened. There remain only a few light spots distributed about the centre of the substance. In observations using a tuning fork in the beginning, while the vibrations of the fork are still sufficiently strong, one also observes several circles of equal double refraction. Upon very intense excitation (experiments using a motor approximately 100 r.p.s., the maximum speed obtainable with our motor) such circles appear in great numbers and the picture becomes very similar to that observed upon the application of pressure to the watch glass.

From these preliminary indications it is difficult definitely to state that we have resonance at these frequencies; however, it is very pro-

bable that this is the case.

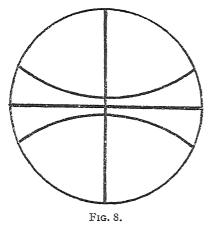
One might have reason to believe that the source of these oscillations is the watch glass, but neither the change of its mass, dimensions nor different methods of damping gives an indication that the origin of the

oscillations is in the glass. Upon intensive excitation by the motor the liquid appeared as if in a boiling state.

We note further that, with a magnetic field of sufficient strength, the damping of the oscillations is considerably diminished. The light spots obtained by shock excitation are preserved over indefinitely long periods of time in the presence of intense magnetic fields. To deduce

intense magnetic fields. To deduce from the above observed phenomena any definite conclusions is as yet not possible, but it seems to us that their investigation might

be very helpful in the study of swarms and their nature. For in-



stance, the small number of vibrations per second lends strength to the theory of swarms. If one assumes that the elastic properties of an anisotropic liquid are determined by the constant, A, in equation (I) of Ornstein, and that the volume of a swarm is of the order of 10<sup>-15</sup> cm.<sup>3</sup>, the velocity of propagation of the elastic waves may approximately be assumed to be a few hundred meters per second or somewhat less. One may also draw certain analogies to the Barkhansen effect in which we observe certain magnetisation discontinuities which occur in a fine wire (Sixtus and Fonks). However, it is yet too early to speak definitely of this, in the absence of quantitative measurements.

In conclusion we wish to remark that we put forward the above material only as a subject that might, perhaps, be of use as an addition to the material for discussion at the Conference.

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# NEW ARGUMENTS FOR THE SWARM THEORY OF LIQUID CRYSTALS.

By L. S. Ornstein and W. Kast (Utrecht).

Received in German on 20th January, 1933, and translated by HELEN D. MEGAW.

Before dealing with some new measurements on liquid crystal melts of p-azoxyanisole that have furnished new arguments for the swarm theory, we shall give as introduction a short summary of the main features of the theory and the most important evidence in its favour.

The spontaneous anistropy which characterises liquid crystals must be due to an arrangement of the molecules. X-ray photographs have now shown that no lattice arrangement exists, and this has recently been confirmed by one of us (Kast), who, using strictly monochromatic Cu-radiation selected from the resolved spectrum, obtained photographs (not yet published) which showed that, except for the rather smaller intensity throughout, no difference exists between the crystalline liquid phase and the amorphous liquid phase. M. and G. Friedel 1 have now introduced the conception of mesomorphous structure. Vorländer and Bose had already worked on the assumption that the molecules have a tendency to set parallel, and this parallel-setting, in which each molecule must be displaced in the direction of its axis, and rotated about that axis, by random amounts, here appears as the lowest order of the mesomorphic structure, the nematic structure.

It is not implied, however,—and here we come to the formulation of the Swarm Theory—that the structure stretches uniformly over the whole macroscopic preparation. A large number of experimentally observed facts suggest rather that it exists only in smaller agglomerations or groups, comprising about 100,000 molecules, which groups lie with their principal directions irregularly disposed, and have interactions much weaker than those between molecules in the same group. Any further arrangement is due to external forces. We might speak of a kind of polycrystalline structure, and we can in fact treat these groups as independent micro-crystals, in cases where the processes concerned are of short duration compared with the individual existences of the groups. But, as is shown by the kinetic considerations we discuss later, the length of their individual existences is limited by diffusion-like processes, and so we prefer to call these groups "swarms."

The first exact mathematical treatment of the Swarm Theory was given by Ornstein and Zernike 2 for systems in the neighbourhood of the critical point. They showed that the correlation of the density deviations in the neighbourhood of the critical point became very large,

M. and G. Friedel, Ann. Physique, 18, 273, 1922.
 L. S. Ornstein and F. Zernike, Physik. Z., 19, 134, 1918.

and hence they succeeded in giving a formula for the opalescence up to the critical point, which, in contrast to the Einstein-Smoluchowski formula, does not become infinite at the critical point. In detail, the correlation occurs as follows. The relationship between the density of neighbouring volume elements, being dependent according to Boltzmann's principle on the potential energy of the molecular forces, like that is directly effective only for very small distances, of the order of molecular dimensions. For example, if at a point P1 a known density deviation is given, then the most probable density (or density fluctuation) is only influenced by this over quite a short distance. But, in addition to the direct effect, there is an indirect effect. For example, if the point P<sub>2</sub> is directly influenced by P<sub>1</sub>, and similarly P<sub>3</sub> by P<sub>2</sub>, then  $P_3$  is also influenced indirectly by  $P_1$ , since the density at  $P_2$  depends on that at P<sub>1</sub>. Therefore the density at P<sub>3</sub> is indirectly dependent on the density at P<sub>1</sub>, and similarly also with a point P<sub>4</sub> which is directly influenced by P3. The further one goes from P1 the weaker, naturally, become these indirect probability effects; and as Ornstein and Zernike have shown, one can define a mean effective radius of indirect influence. The ranges over which this indirect correlation exists are the swarms of density-fluctuations.

If we now apply these considerations to liquid crystals, the dense packing of the molecules in the liquid makes it possible to neglect density-fluctuations. We now consider, instead, fluctuations of direction. We assume that the molecules, by reason of their elongated form (and if necessary also their permanent dipole moment) exert on one another rotation moments which tend to set them parallel. Further, two molecules only exercise direct mutual influences on their positions when they are quite close together; but through the indirect influence we get larger fields in which the directions of the molecules are nearly the same, and these are the swarms of direction-fluctuations. We shall not discuss the orienting forces in detail, but we may say that the hypothesis for the formation of such swarms presupposes an unsymmetrical shape of the molecules. Monatomic liquids, or those with spherically symmetrical molecules, can never form such swarms. On the other hand, from co-operation of the rotation-moments of dipoles, which have a much larger effective radius, mathematical difficulties as to convergence arise, if, indeed, a screening effect does not occur. The fact that the mutual attractive or repulsive forces of the dipoles are effective only over small distances tends to make the molecules link on end to end rather than lie side by side. The swarm will therefore have an anistropic shape whose long axis coincides with the direction of the dipole.3

A liquid which, because of the structure of its molecules, has a tendency to swarm-formation, will therefore consist of swarms which

$$f(x'-x,y'-y,z'-z) \left\{\cos\phi\cos\phi' + \sin\phi\sin\phi'(\cos\psi\cos\psi' + \sin\psi\sin\psi') - 3(\cos\phi\cdot l + \sin\phi\sin\psi\cdot m + \sin\phi\cos\psi\cdot n + \cos\phi'\cdot l + \sin\phi'\sin\psi'\cdot m + \sin\phi'\cos\psi'\cdot n)\right\}.$$

The symbols have the same meaning as they have there; l, m and n are the direction-cosines of the line of junction. The conclusion reached earlier, however, is not altered in any way.

 $<sup>^3</sup>$  One of us, elsewhere (L. S. Ornstein, Z. Krist., 79, 117, 1931), starting from the potential energy of two molecules which exert a rotation-moment on one another, has given a mathematical treatment of the direction-swarms. It is better to put for the value of the potential energy

are of approximately equal size. The swarm-direction (or direction of the molecules in the swarm) will, however, be different from one swarm to another, and transition ranges will occur between the separate swarms. If now at a given instant the distribution of molecules between the swarms is known, it will only alter very slowly, because that involves a sort of diffusion process. Hence for many purposes a swarm may be considered as an independent elementary particle, e.g., one may even speak of the Brownian movement of the swarm as a whole.

2.

As important evidence for this idea of swarms in liquid crystals, we may call to mind a series of measurements made in the Utrecht Institute.

The marked turbidity characteristic of liquid crystals makes it plausible to assume that their elementary ranges are disordered. But, more than this, the agreement of the measurements of transparency 4 with the swarm theory is a quantitative one. Ornstein and Zernike 5 have calculated the light scattered by a medium where arbitrary gradients of refractive index occur, and have shown that the transparency depends on the product  $\omega^2 d$ , where d is the thickness of the layer and  $\omega^2$  the mean square of the scattering angle for unit length of the path traversed, a quantity which is proportional to the square of the double refraction. Experimentally, Miss Riwlin found, varying the wave-length of the light and the thickness, that for the same transparency the values of  $(n_1-n_2)^2d$  were constant to within less than I per cent. We are therefore concerned with an aggregate of irregularly arranged doubly-refracting regions.

In many cases where one works with thinner layers one sees no turbidity, but larger regions which extinguish uniformly under the polarising microscope. We shall now show that these larger ordered regions only come into existence under the action of external forces. It is characteristic of liquid crystals that, for example, very small fields suffice for magnetic orientation; and similarly very small electric double layers or capillary forces will suffice to introduce at the edge of the preparation a far-reaching arrangement of the swarms, which extends by correlation for a few hundredths of a millimetre depth into the preparation. Miss Riwlin's measurements give a good example of this also. When the preparation was obtained by melting the solid, it always acted as if its thickness were 0.04 mm. less than if it had been obtained by cooling from the clear liquid. This shows that when it is obtained from the solid, the orientation of the solid crystals with respect to the walls gives rise to a layer 0.02 mm. thick on each side of the preparation which lets nearly all the light through and is therefore regularly ordered.

But even when the preparation is obtained from the liquid a similar arrangement is set up from the outside inwards. This is shown by the extinction experiments of Moll and Ornstein 6 in a magnetic field. a strong field perpendicular to the surface of the bulb the transparency, and therefore the arrangement of the swarms, is greater than in the absence of the field. But after the removal of the field it is actually

R. Riwlin, Dissertation, Utrecht, 1923.
 L. S. Ornstein and F. Zernike, Proc. Acad. Amsterdam, 21, 115, 1917.
 W. I. H. Moll and L. S. Ornstein, Versl. Acad. Amsterdam, 25, 682, and 112,

<sup>1916-17.</sup> 

much less than in the initial state. Hence it follows, in the first place, that we are not dealing with a structural relationship over the whole layer; because in that case, after a temporary deformation of the structure by the magnetic field, the old structure, and therefore the old transparency, would reappear. Secondly, it follows that a certain arrangement must have existed in the initial state. We then understand the photometer curves of the transparency given in Fig. 1 to mean that the magnetic field destroys the arrangement with axes parallel to the wall but random azimuth, which predominates in the original state (A) (lower portion of the curve), and changes it to an arrangement with vertical axes (B), which is more complete in strong fields, but less in weak ones, than the original state. When the field is removed, the arrangement of the swarms breaks up completely; a very opaque state (C) is then obtained, which, however, is not stable, but generally

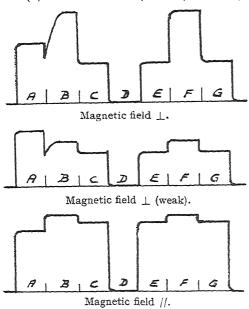


Fig. 1.—Light-Transmission of Liquid-crystalline p-Azoxyanisol.

goes over after some hours into the initial state arranged from the outside inwards. we are really concerned here with an arrangement with axes parallel to the wall is shown by measurements with parallel magnetic field. Here (B) the field only slightly improves arrangement of A, by re-orienting the azimuths, and this better arrangement is to a large extent preserved after the removal of the field (C), and is stable. In this experiment, too, the arrangement from the outside occurs to a greater extent when the preparation is obtained from the solid. In this case one obtains in strong fields

the same curve as with the preparation from the liquid in weak fields.

In these thin layers at the edge, and in these only, we have now in fact an extensive structural relationship; in thin microscopic preparations it may frequently extend throughout the whole preparation. This is shown by the experiment of Moll and Ornstein, which demonstrates the heat effect of magnetic orientation. This succeeds only if a silver plate is hung in the melt to act as a thermo-element, and the field applied perpendicular to it. It is then found that after the application of the field a slow heating of the plate occurs, and after its removal a slow cooling. From the fact that a parallel field alone has no effect, but when applied in conjunction with a vertical field it accelerates the cooling, it is apparent that adiabatic temperature changes from the

deformation of the outside layers are involved. Clearly the outside layers manifest themselves in the same way in the peculiar effect of the magnetic field strength on the optic axial figure, which has been observed by van Wijk.<sup>8</sup> The optic figure is not steadily improved by increasing field-strengths; instead, it is very prominent for certain field-strengths and disappears for others. This may be explained by considering quantitatively the arrangement of the swarms at the outside. In the interior all the swarm axes lie parallel to the field, but at the outside they lie at an angle depending on the interaction of the surface and the magnetic field. Hence with increasing field strength the path difference in the outside layers alters, and an optic figure only occurs when it is equal to an integral number of wave-lengths. The expression obtained for

the "optical thickness" of the edge layer is  $\delta = \frac{K}{H^{\alpha}}$ , where K is a constant

depending on the material and treatment of the bulb; the index  $\alpha$ , in accordance with the hypothesis of magnetic rotation-moments of diamagnetically anisotropic particles, is nearly equal to 1. The value of the thickness  $\delta$  for 1200 gauss is 0.01 mm., for 10,000 gauss 0.002 mm.

All these experiments, then, show that invariably the molecules of the liquid are arranged only into individual swarms, and that any more extensive arrangement has its origin in external forces, whether these are produced by arbitrarily applied fields, or arise by themselves at the surface of contact between the melt and solid bodies, particularly glass. We now turn to experiments that give information as to the size of the swarms. Up to the present we could only make the qualitative statement that the reason why weak fields have so large an arranging effect is that they attack not single molecules but the whole swarm. We now know from the experiments of Foëx and Royer 9 that the molecules are diamagnetically anisotropic with  $\mu_1 - \mu_2 \approx 10^{-6}$ , and from the dielectric measurements of one of us 10 in a magnetic field that they are also dielectrically anisotropic with  $\epsilon_1 - \epsilon_2 = -0.1$  (the subscript I applies to the direction along the axis). From the calculation of the dielectric constant as a function of the magnetic field strength, the constants of the magnetic rotation moment of the swarm are found:

$$(\mu_1-\mu_2)v \gtrsim$$
 10<sup>-21</sup>, hence  $v \gtrsim$  10<sup>-15</sup> cm.<sup>3</sup>.

In this, the assumption is made that on account of the thickness of the layer used only the opposing effect of the heat motion enters the calculation. The figures thus arrived at indicate that in such a swarm about 106 molecules are held in parallel positions. A further estimate of the size is given by orientation experiments in an electric field. The dielectric measurements of Ježewski 12 had already suggested the probable existence of a permanent dipole along the axis of the swarm, and the orientation of the swarms parallel to the lines of electric force was proved directly by one of us, 13 by means of X-ray photographs. These X-ray pictures show, in an electric as well as in a magnetic field, 14 a splitting of the broad interference ring into two arcs whose centre of gravity

A. van Wijk, Ann. Physik (5), 3, 879, 1929.
 G. Foëx and L. Royer, C.R., 180, 1912, 1925.
 W. Kast, Ann. Physik (4), 73, 145, 1924.
 V. Fréedericksz and A. Repiewa, Z. Physik, 42, 532, 1927.
 M. Ježewski, Z. Physik, 51, 159, 1928, and 52, 878, 1929.

W. Kast, Z. Physik, 71, 39, 1931 and 76, 19, 1932.
 W. Kast, Ann. Physik (4), 83, 418, 1927.

lies in the direction perpendicular to the field. This leads inevitably to the assumption of a dipole moment in the swarm-direction, since the dielectric anisotropy must itself bring about a setting of the molecules across the lines of electric force. Thus we are here concerned with a case similar to that of molecules with negative Kerr constants, where the direction of the greatest polarisability (i.e., of the induced dipole moment) and of the permanent dipole moment are at right angles. In consequence two rotation-moments appear in the electric field, one turning across proportional to  $(\epsilon_2 - \epsilon_1)vF^2$  and one along the length, proportional to pF. Since the X-ray picture for a field-strength of 7200 volts/cm. still shows perfect parallel formation, we obtain the inequality

$$pF \gg (\epsilon_2 - \epsilon_1)vF^2$$
;

and for F=24 e.s.,  $v=10^{-15}$  cm.<sup>3</sup>, and  $(\epsilon_2-\epsilon_1)=0\cdot 1$ ;  $p\gg 10^{-14}$  e.s. This is more than  $10^4$  molecular dipole moments, whose magnitude <sup>15</sup> is fixed as  $2\cdot 3\times 10^{-18}$  e.s., and the consequence is, as is required by the swarm theory, that the molecular dipoles must lie in the swarm so that they add.

3.

The new investigations follow on from the separation of the two electric rotation moments which was carried through by one of us <sup>16</sup> with alternating fields of increasing frequency.

with alternating fields of increasing frequency.

In the experiments so far the X-ray picture was obtained in alternating fields of different frequency. Up to about 25,000 oscillations per second the picture did not change; above that, the fibre character of the picture became more marked. Hence the time of relaxation of the particles is  $\frac{1}{25000}$  seconds. Above that they no longer follow instantaneously. At about 300,000 oscillations per second, the splittingup has completely vanished. This marks a second critical time, that which the particles need to turn through 180° under the influence of the field; here the phase difference between the alternating field and the movement of the dipoles has the value 180°. At yet higher frequencies, the dipoles no longer reach the position parallel to the field during one reversal of the field, and so only oscillate about their equilibrium positions, which are independent of the frequency and in which the induced dipole lies in the direction of the field. Correspondingly, the diagram again shows a fibre character, but now with the fibre direction perpendicular to the field. The measurements therefore give a relaxation time of the order of 10<sup>-5</sup> sec. as against 10<sup>-11</sup> sec. for ordinary molecules. It is not yet possible, however, to enter into further quantitative considerations, because it is not easy to see at a glance the nature of the frictional mechanism, which cannot, indeed, without unduly forcing it, be visualised as Stokesian friction. There are, however, particular cases where the relaxation time is found to be very low for normal viscosities throughout (about 135 referred to water at 0° C. as 100), so that to obtain times which can be measured with the oscillation apparatus it is necessary to raise the viscosity artificially by adding oil at low temperatures. The importance of this experiment does not, however, merely lie in its determination of at least the order of magnitude of the swarms; it is rather that the introduction of a friction dispersion makes probable the separate existence of swarms and the uniformity

J. Errera, Phyzik. Z., 29, 426, 1928.
 W. Kast, Z. Physik, 71, 39, 1931.

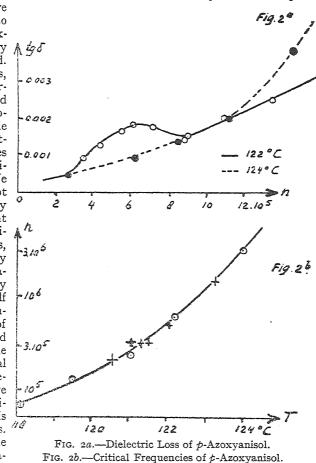
of their size. It appeared, therefore, desirable to obtain further confirmation of these results by a more direct method.

For this purpose, measurements were made of the dielectric loss in a condenser filled with liquid crystals of p-azoxyanisol over the frequency range 5000 to 3,000,000. The dielectric loss plotted against the angular frequency  $\omega$  gave a hyperbola, so long as only a pure con-

duction loss was involved, on account of the relation tan  $\delta = \frac{1}{\omega RC}$ ;  $\omega$  tan  $\delta$  is constant. This is the same whether polar or non-polar

molecules are concerned, SO long as the relaxation frequency A to 5 is not exceeded. If that happens, the phase-difference introduced between the motion of the dipole and the alternating field gives rise to an additional loss. We do not attempt give any further account of the experimental details, except to say that the relaxation frequency must show itself by the commencement increased and the second critical frequency referred to above by the maximum of this additional loss. "" Now the value of the relaxa-

tion frequency



depends on the magnitude of the forces which resist turning, and therefore in some way on the size of the particles. But the size of the swarms decreases with rise of temperature, as determined from measurements of their double refraction and their diamagnetic and dielectric anisotropy; hence we can arrange the measurements so that we either maintain a fixed temperature and look for the relaxation frequency by varying the frequency, or else apply a fixed frequency and vary the temperature.

We have carried out measurements by both methods, and found maxima of dielectric loss that agree in the temperature range between 118° and 124° C. for frequencies from 70,000 to 3,000,000. Fig. 2a shows two loss curves for varying frequency at temperatures 122° and 124° C. The distinct general increase of loss with increasing frequency occurs also in experiments with the condenser empty, and may therefore be subtracted. The occurrence of a frictional dispersion for frequencies of the order of  $10^5$  is thereby confirmed as expected. But the very surprising thing is the extraordinarily large variation with temperature (as shown in Fig. 2b) of the frequency at which the friction dispersion occurs. It confirms the conclusion already mentioned, that we may not visualise it as a Stokesian friction. In that case, from this large variation with

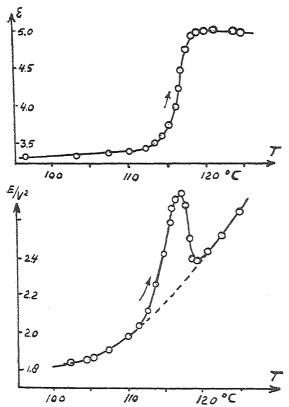


Fig. 3.—Upper Diagram: Dielectric Constant of p-Azoxyanisol. Lower Diagram: Dielectric Loss preparation, of p-Azoxyanisol. way throu

temperature, having regard to the normal small alteration viscosity, should have to postulate a very large alteration of the size of the swarms, such as is not even approximately consistent with other experiments. For example, it appears from the measureof Miss ments Riwlin 4 that the transparency creases slightly with increasing temperature, although the double refraction decreases. the formula

$$D = C(n_1 - n_2)^2 d$$

it can thus be seen that the constant C, i.e., the number of differently oriented layers which the light traverses on its way through the preparation, increases rather more rapidly than the

square of the double refraction diminishes; but it changes at most by a factor of 3 over the whole range in which liquid-crystalline melts exist. It is therefore impossible that the linear dimensions of the swarms should change more than this; and the same estimate is reached from the values of  $\mu_1 - \mu_2$  and  $\epsilon_1 - \epsilon_2$  derived from the measurements of dielectric constant in a magnetic field.<sup>17</sup> Hence we see that the explanation of the large variation with temperature must lie in a friction mechanism of such a kind that the swarms, in turning, knock against one another

and are deformed. Then the forces resisting turning involve the elastic properties of the swarm, which may vary rapidly with temperature.

From the measurements with varying temperature we found an interesting new effect. After the loss-maximum expected for a given frequency had been passed through somewhere in the liquid-crystal range, there appeared a second maximum, just before crystallisation occurred, which was very nearly in the same place for all the frequencies used. Fig. 3 shows this effect, as it occurred for uniformly increasing temperature at a frequency of 106. The upper curve gives the dielectric constant for the same temperature-scale, and shows that the anomalies occur just at the melting-point. For these phenomena the only possible explanation is that here there occur again swarms of the same size as those which had been present in the ranges where liquid crystals exist, or, that here temporary swarms occur, of the same size as appear again later in the liquid-crystal melt. We think that those molecules, which in the melt do not belong to swarms but lie in the spaces between them, become associated in the immediate neighbourhood of the melting-point with swarms of quickly altering size. We shall deal later with the importance of this phenomenon for the melting-point; but here we are only interested in the conclusion, that, as shown by the magnitude of the effect, the spaces between the liquid-crystal swarms are of considerable size, about the same order of magnitude as the swarms themselves. This, however, raises no difficulties in our calculation. For example, Hermann 18 has concluded that those molecules which do not lie in the swarms must, in a magnetic field of any considerable strength, cause the appearance of a faint complete ring in the X-ray diagram, but this is not so. For if all the swarms were oriented parallel, then the spaces between would lose their identity. The parallel arrangement would spread out from the swarms over what were the spaces between, and it would perhaps be interesting to follow how the breaking-up of the general arrangement in swarms happens when the field is removed. And this even obviates the difficulty that one might perceive in the absence of anomalies of dielectric constant corresponding in a normal way to friction dispersion. Thus for one swarm there occur in the layers between, which are of the same order of magnitude, the same number of 105 separate molecules which do not show frictional dispersion at this place. Moreover, one must consider that, on account of the occurrence of saturation phenomena for the orientation of the dipoles during one alternation, the dielectric constant has no longer a constant value.

4.

The effect here described, in which shortly before crystallisation even those molecules which do not lie in swarms in the liquid-crystal melt proceed to form swarms of rapidly increasing size, must not be confined to the liquid-crystal melt.

The same temporary increase of the dielectric constant which Errera <sup>15</sup> has observed at the melting-point of p-azoxyanisol and which we may connect with this effect is also indicated in ordinary dipole liquids, e.g., in water. In both cases it is limited to very low frequencies. Errera finds it with 680 oscillations per second, but not with 300,000; and the dielectric constant of ice at the melting-point for frequencies

of the order of 106 is stated to be about 2, but for frequencies of the order of 100 to be from 80 to 90.

1. TABLE—DIELECTRIC CONSTANT OF p-AZOXYANISOL FOR FREQUENCY 680.

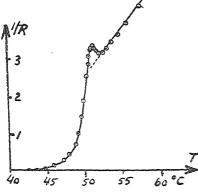
151° C.	5.2	117° C.	5.4
145	5.2	116.6	12.6
136	5.3	116.4	11.5
122.8	5.3	115.8	7.2
119	5.4	111.2	3.8

TABLE. II-DIELECTRIC CONSTANT OF ICE NEAR THE MELTING-POINT.

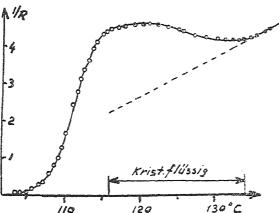
− 2° C.	Frequency 40-80	93-9	P. Thomas, Physic. Rev., 31, 278, 1910.
0	100	78 ∖	J. Dewar and J. A. Fleming, Proc. Roy.
0	107	2 ∫	Soc. London, 61, 2, and 316, 1897.

We therefore extended our measurements of dielectric loss to ordinary dipole liquids, and next investigated benzophenone ( $C_6H_5$ —C— $C_6H_5$ ).

Benzophenone has a very strong dipole moment, as follows from the



large increase of dielectric constant (from 3 to 12) at the melting-point. The measurements were difficult because of this large change of dielectric constant, and also because with decreasing temperatures there is much super-. cooling. The expected effect was, however, indicated. To control the conductivity, because of its big influence on the loss, we proceeded to make provisional measurements of conductivity. The arrangements were such that a potential of 6 volts was applied



every time until the galvanometer reversed again; this ballistic deflection was then From this read. it appeared that the conductivity followed culiar course the melting-point, which we could show to be compatible with the temporary existence of swarms. The conductivity at the meltingpoint increased, first slowly, then

Fig. 4.—Upper Diagram: Conductivity of Benzophenone (6 volts).

Lower Diagram: Conductivity of p-Azoxyanisol (6 volts).

more steeply. Thus, when the temperature-time curve shows the end

of the melting process, it still does not bend down again at once, but increases steeply for a short time, goes through a pronounced maximum, and finally passes over into a straight line which corresponds to the normal temperature gradient of conductivity (Fig. 4). Here, of course, we are concerned with conductivity by foreign ions, and the maximum therefore indicates a temporary ionic mobility which is abnormally large. In this connection, we remember that in liquid-crystalline p-azoxyanisol 19 a corresponding rise in conductivity can be produced by magnetic or electric orientation of the swarms, and we therefore conclude that in benzophenone in quite a small temperature range above the melting-point there exist swarms which have so large an electric moment that they can be appreciably arranged by 6 volts in  $\frac{1}{2}$  mm. or 120 volts per cm.

As a control we have performed the same experiment on p-azoxyanisol, for which we find experimentally, over the whole range in which it is an anisotropic liquid, the same course of the conductivity as for benzophenone at its melting-point (Fig. 4). We have now evaluated these curves; we find the difference of conductivity relative to the straight line of the normal liquid range produced backwards, and this shows that the curves for p-azoxyanisol and benzophenone can be brought into coincidence by merely adjusting the temperature scale. If we now add the rotation moment to the dipole moment of the swarm, and write  $\sigma_1$  for the conductivity in the direction of the swarm axis and  $\sigma_2$  for that in both directions perpendicular to it, we can calculate the increase in conductivity by Boltzmann's hypothesis. We obtain the same formula that was previously derived by one of us 20 for the change in conductivity in a magnetic field, using the assumption of a permanent magnetic moment of the swarm. In consequence of the conductivity anisotropy of the swarms, a rotation moment will of course occur, which gives rise to an apolar setting of the swarms in the direction of the electric field. But, just as was the case for the rotation moment due to the dielectric anisotropy, this can be neglected in comparison with the rotation moment from the strong permanent dipole of the swarms. We thus obtain :-

$$\Delta \sigma = \frac{2}{3} (\sigma_1 - \sigma_2) \left\{ I - \frac{3 \coth C}{b} + \frac{3}{b^2} \right\}$$
$$b = \frac{pf}{bT}.$$

where

We now treat  $(\sigma_1-\sigma_2)$  as approximately independent of temperature; then only the expression in the bracket depends on the temperature, because the dipole moment is connected with the size of the swarm, which depends on the temperature. The absolute temperature, which appears directly in b, only changes from 391° to 407° and can therefore be left out of consideration. By comparison of the calculated curve  $\Delta\sigma=$  const. f(b) with the experimental curve  $\Delta\sigma=g(T)$ , we now obtain b and hence also the dipole moment p as a function of the temperature (Fig. 5). This result is in excellent agreement with our earlier estimate  $p\gg 10^{-14}$  e.s.; because we find in the neighbourhood of the meltingpoint 200  $\times$   $10^{-14}$  and in the neighbourhood of the clearing-point

 $<sup>^{19}</sup>$  Th. Svedberg, Ann. Physik (4), 44, 1121, 1914; and W. Kast, Ann. Physik (4), 73, 145, 1924.  $^{20}$  L. S. Ornstein, Ann. Physik (4), 74, 445, 1924.

 $10 \times 10^{-14}$ . A more accurate estimate of the extreme value is not possible, since the experiments were done with steadily increasing temperature and therefore there was a temperature fall in the melt. From the known size of the molecular dipole moments,  $2 \times 10^{-18}$  e.s., we deduce that the number of molecules contained in a swarm is from  $100 \times 10^4$  down to  $5 \times 10^4$ ; and the same values apply also for benzophenone, where, however, they cover a very small temperature range immediately above the melting-point. Corresponding to the alteration, by a factor of 20, of the number of molecules in a swarm, the linear dimensions of the swarm will alter by a factor of about 3, a value which agrees very well with the estimate given above.

It must now, of course, be shown that liquids not containing dipoles do not give this effect; because even if the dipole moment were not essential for swarm formation, its presence is the condition which makes possible the orientation of swarms in weak fields. This control raises a new and interesting difficulty. A molecule such as benzene has, of

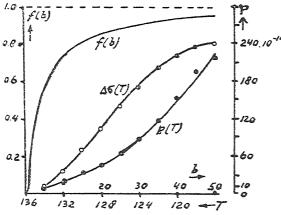


Fig. 5.—Dipole Moment of p-Azoxyanisol.

course, no dipole moment as a whole; but it has six local moments which in general compensate externally. now if, in solution, or perhaps even at the melting-point, the molecules come particularly closely together, then the local dipoles can be effective. Thus, Isnardi 21 that there is anomalous increase the dielectric constant of liquid

benzene shortly before the melting-point; and we are indebted to Professor Holst of the Philips-Eindhoven Company for the information that Dr. v. Arkel has made similar observations in benzene solutions. It is very characteristic of this effect that it disappears when the hydrogen atoms of benzene are substituted by F or Cl atoms. These large atoms prevent a sufficiently close approach of the molecules. On account of this difficulty we have not yet been able to make a valid control experiment with substances not containing dipoles. Naphthalene ( $C_{10}H_{10}$ ) shows the conduction anomaly similarly, though to a still smaller degree than benzophenone, but this is understandable from what has just been said about benzene. On the other hand, experiments with carbon tetrabromide have proved impracticable at present because of the readiness with which it vaporises even from the solid state.

5-

We can summarise these considerations about the melting-point by saying that apparently every liquid which has not spherically symmetrical molecules forms swarms, in the immediate neighbourhood of the melting-point, of the same kind as are stable for liquid crystals over a larger temperature range. We now make some observations

upon the clearing-point.

The objection is frequently urged against the swarm theory of liquid crystals that it cannot account for a sharp point of transition from ordinary liquids. This is due to a misunderstanding of the Phase Theory. The Phase Theory always gives sharp transitions when, for two modifications with different internal potential energies, at a given temperature and pressure, the thermodynamic potentials per unit mass are equal. These values of the temperature and pressure define the critical point at which the two phases co-exist. Here, fluctuation phenomena have, as a whole, no effect. In a kinetic treatment in which density deviations or deviations from ideal lattice structure do have an effect, their influence ceases as soon as one turns to the derivation of equilibrium conditions. This is due to the fact that, kinetically expressed, thermodynamics is a science of mean values, and in considering mean values fluctuation phenomena are eliminated. One can hardly speak of the influence of fluctuations on the (macroscopic) pressure, and it is no more legitimate to speak of their influence on the entropy or thermodynamic potential.

To decide, therefore, the existence of a sharp transition point in the to determine whether it is possible to construct two different liquid modifications with different internal potential energies. Now it is easy to think of two possibilities; the first as described above, with swarms of molecules oriented parallel, and the second where the needleshaped molecules stick confusedly in all directions. Both the energy of shape and the dipole energy would be different, and they would also have different specific volumes, and therefore different internal energies of the molecular attractive forces (van der Waals' forces). From our knowledge of liquids derived from X-ray photographs, particularly those of Stewart, we know, however, that swarms in our sense of the word exist even in ordinary liquids. In one of his latest papers Stewart 22 has summed up the properties of the so-called cybotactic groups, which include a few hundred or thousand molecules, and possess temporary individual existences, badly defined limits, an optimum size, internal regularity, and anisotropic extension, all properties which we attribute to our swarms. It is only the number of molecules which is smaller. It is very interesting that in this respect cybotactic groups form a continuous series with nematic groups at the clearingpoint. Thus we have molecular structures which are broken up into swarms in the amorphous liquid phase as well as in the liquid-crystal phase. Then the clearing-point means for the swarms the transition from one structure to another with higher internal potential energy. In particular, it is possible to say of these structures that in the nematic group the anisotropy of the single molecules is considerably magnified, but in the cybotactic group it is to a large extent cancelled out. If we now think of the molecules in nematic swarms as parallel, and with their dipole moments parallel, then we can check this assumption if we think of the molecules, either singly or in small groups, as lying antiparallel or crossed, still, of course, without any arrangement of their centres of gravity.

<sup>&</sup>lt;sup>22</sup> G. W. Stewart, Physic. Rev. (2), 37, 9, 1931.

#### Summary.

We shall sum up the points considered in a number of statements that may perhaps serve as a basis for discussion:—

(r) Liquid crystals are aggregates of sub-microscopic homogeneous

ranges, the so-called swarms, in which the molecules all lie parallel.

(2) The structure is to be visualised as of a polycrystalline nature; the swarms have an individual existence of considerable duration.

(3) The swarms lie perfectly irregularly; their axes are distributed at random.

(4) Any further arrangement of the swarms into larger homogeneous

ranges is caused by external forces.

- (5) At the surface of contact of the melt with solid bodies there occur forces, due to electric double layers and capillarity, which give rise to an arrangement of the swarms up to a few hundredths of a millimetre deep in the layer. The special phenomena in thin layers have therefore no bearing on the nature of liquid crystals.
- (6) The rotation moments of electric and magnetic fields are large because they act, not on single molecules, but on the whole swarm. Quantitative experiments on orientation give the number of molecules in a swarm as of the order of 105.
- (7) The swarms are doubly refracting, diamagnetically and dielectrically anisotropic. The axis of the swarm is the direction of least diamagnetism and least electric polarisability.
- (8) The swarms possess, in the direction of their axis, a permanent electric moment of about 10<sup>5</sup> times the value of the molecular moment. Consequently saturation effects occur even in weak electric fields.
- (g) From the effect of the orientation of the swarms on the mobility of foreign ions in the melt, the size of the swarms can be calculated over the whole range of existence of liquid crystals of p-azoxyanisol; they are found to include from 10  $\times$  10<sup>5</sup> to 0.5  $\times$  10<sup>5</sup> molecules.
- (10) From X-ray photographs in an alternating electric field, as well as from measurements of dielectric loss, it is seen that the swarms show the phenomenon of frictional dispersion for frequencies of the order of 105 to 106.
- (11) The critical frequency varies extremely rapidly with temperature, much more than can be explained by the decrease in size of the swarms. This indicates that a resistance to the turning of the swarms arises from the way they knock against one another and are deformed, the magnitude of which depends on the elastic properties of the swarms.

(12) The swarm formation comes about, in the first place, because of the unsymmetrical shape of the molecules. The dipole moment only comes into consideration secondarily, but must act in such a way that the

swarms have an elongated shape.

(13) Several liquid modifications with sharp inversion points can exist if there are different liquid molecular structures with different internal potential energy. It is, however, immaterial whether these structures are homogeneous over the whole volume or are broken up into swarms.

(14) The nematic swarm and the cybotactic swarm represent twoaspects of such structures. In the first the molecules lie so that their anisotropies are magnified; in the second, which must have a high internal potential energy, so that the molecular anisotropies are to a large extent cancelled out.

# THE EFFECT OF A MAGNETIC FIELD ON THE NEMATIC STATE.

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(Experimental Section in collaboration with W. Eisenschimmel.)

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Two fundamentally different hypotheses have hitherto been used to account for the changes in nematic systems in a magnetic field; these are the Swarm Theory and the Distortion Theory (Verbiegungstheorie). It is extremely important to decide which is the correct one, not only for the particular problem dealt with in this paper, but for the whole general question of the structure of these phases.

The experimental evidence for the swarm theory depends essentially on the changes of dielectric constant in magnetic fields, to which Ornstein <sup>1</sup> applies Langevin's theory of ferromagnetism, while Fréedericksz 2 uses Gans's theory of diamagnetism. A quantitative comparison with the distortion theory has not hitherto been possible, as the necessary mathematical treatment was not available. This is given in what follows.

A theory of distortion in a magnetic field was given some years ago by the author.3 In that a case was considered which involved no changes in the dielectric constant. We shall consider it briefly. The following assumptions are made. (I) The whole substance tends to take up a position such that the axial direction at every point is the same. (2) Any force acting so as to disturb this state where the directions are uniform causes a distortion in which the direction changes continuously until a restoring force of an elastic nature holds the applied force in equilibrium. (3) At surfaces of solid bodies (e.g., glass or metal) the positions at first assumed are almost unchangeable.

Let us now consider a case in which the substance is placed between a fixed plate and one which can be rotated; and assume that at both plates it orientates itself with the principal axes parallel. Then when no forces act, the movable plate sets with its direction of axis parallel to that of the fixed plate. A torque D acting on the movable plate causes a rotation which increases with the turning-moment. For small distortions, the angle  $\phi$  between the azimuths at the upper and lower plates will be proportional to the turning-moment, i.e., it will obey Hooke's Law. The elastic resistance is directly proportional to the area q of the layer, and inversely proportional to its thickness z. This gives the relation

The quantity  $k_t$  corresponds to a kind of torsion modulus, and has the dimensions of a force; hence it is expressed in dynes. It can be seen that there is an analogy with the deformation of ordinary solid bodies.

L. S. Ornstein, Ann. Physik, 74, 445, 1924.
 V. Fréedericksz and A. Repiewa, Z. Physik, 42, 532, 1927. <sup>3</sup> H. Zocher, Physik. Z., 28, 790, 1927.

though the deformation is actually of a different nature. It consists of a pure torsion without sheer, which in a solid cylinder only occurs in a line along the axis.

If a magnetic field is now allowed to act on an undeformed layer perpendicular to the axial direction, a state will be arrived at in which the elastic forces are in equilibrium with the magnetic forces. The energy of a layer of thickness dx in a field H is given by

$$dE = q \frac{H^2}{2} (\kappa_1 \cos^2 \phi + \kappa_2 \sin^2 \phi) dx,$$

where  $\kappa_1$  and  $\kappa_2$  are the susceptibilities parallel and perpendicular respectively to the axis of the molecule, and  $\phi$  the angle between the axis and the direction of the field. The increase in the turning-moment in a direction from the movable to the fixed plate is, for each layer,

$$dD = q \frac{H^2}{2} (\kappa_1 - \kappa_2) \sin 2\phi dx.$$

But, from equation (1),

$$D = qk_t\frac{d\phi}{dx}$$
, and  $\frac{dD}{dx} = qk_t\frac{d^2\phi}{dx^2}$ 

hence

$$k_t \frac{d^2 \phi}{dx^2} = \frac{H^2}{2} (\kappa_1 - \kappa_2) \sin 2\phi,$$

$$\therefore \frac{d\phi}{dx} = H \sqrt{\frac{\kappa_1 - \kappa_2}{k_t}} \sqrt{\sin^2 \phi - \sin^2 \phi_0}, \qquad (2)$$

where  $\phi_0$  is the angle between the direction of the field and the axis at the movable surface. For large thicknesses,  $\phi_0 = 0$ , and therefore

$$\frac{d\phi}{dx} = H\sqrt{\frac{\kappa_1 - \kappa_2}{k_t}} \sin \phi.$$

By integrating (2), a relation can be obtained connecting x, the distance from the movable plate, with the axial azimuth:

$$xH\sqrt{\frac{\kappa_1-\kappa_2}{k_t}} = \int_{\phi_0}^{\phi} \frac{d\phi}{\sqrt{\sin^2\phi - \sin^2\phi_0}} \qquad . \tag{3}$$

This integral can easily be brought to Legendre's normal form of an elliptic integral of the first kind:

$$xH\sqrt{\frac{\kappa_1-\kappa_2}{k_t}} = \int_{\psi\sqrt{1-\cos^2\phi_0\sin^2\psi'}}^{\frac{\pi}{2}} \frac{d\psi}{\sqrt{1-\cos^2\phi_0\sin^2\psi'}}$$

where

$$\sin \psi = \frac{\cos \phi}{\cos \phi_0}.$$

We can now imagine a second layer with a second fixed plate so placed above the movable plate that it is a mirror image of the first; it must then necessarily be in equilibrium. Finally, if we make the movable plate infinitely thin, we obtain the case of a layer between two fixed plates. If z is now the total thickness of the layer,

$$\frac{z}{2}H\sqrt{\frac{\kappa_1-\kappa_2}{k_t}} = \int_{0}^{\frac{\pi}{2}} \frac{d\psi}{0\sqrt{1-\cos^2\phi_0\sin^2\psi}} \qquad . \tag{4}$$

for the case, that  $\phi = \pi/2$  at the plates.

The experiment considered here, which we shall call Case III, had not previously been performed, but it will be dealt with in the experimental part of the work. The other two possibilities for the position of the layer in a magnetic field, which will next be discussed, were first investigated in detail by Mauguin,4 who described qualitatively the optical effect. More recently, van Wyk 5 and Fréedericksz 6 have made optical measurements, Jezewski 7 and Kast 8 dielectric measurements. The first possibility is that the position of the substance at the surface is the same as in Case III, but that the field is applied perpendicular to the plate (Case I). The second is that the substance has its axes perpendicular to the plate (so-called uniaxial orientation), and that the field is applied parallel to the plate at any arbitrary azimuth (Case II). In

both these cases, distortion must occur, such that the axis of rotation of the distortion no coincides longer with the x-axis but is perpendicular to The angle made by the axis of the molecules in each layer with the axis of x, at a distance x = 0(i.e., in the middle of the layer), approaches oo in Case I, 90° in Case II, as the field strength The increases. axial lines, i.e., the give lines which the direction of the axis at any point, will be as shown in Figs. 1a and b. The configuration

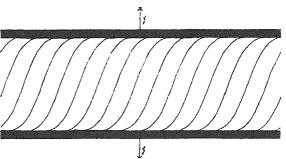


Fig. 1a.—Case I. Axial lines in a magnetic field.  $\phi_0 = 20^{\circ}$ .

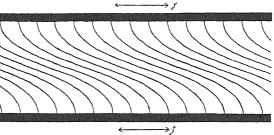


Fig. 1b.—Case II. Axial lines in a magnetic field.  $\phi_0 = 20^{\circ}$ .

will always be given by plane curves if the setting assumed to occur at the surface is homogeneous.

Both these cases are complicated by the fact that the angle made by the axial direction with the x-direction varies, so that even for constant it is not certain whether the torque producing the distortions is the same. The case when the principal axis coincides with the x-direction was previously called by the author "lengthwise distortion" (Längsbiegung), that in which the two directions are at right angles, "fan formation" (Auffächerung) or "cross distortion" (Querbiegung). The

<sup>4</sup> Ch. Mauguin, Comptes Rendus, 152, 1680, 1911.

A. van Wyk, Ann. Physik, 3, 879, 1929.
 V. Fréedericksz and V. Zolina, Z. Krist., 79, 255, 1931.
 M. Jezewski, Z. Physik, 40, 153, 1926.
 W. Kast, Z. Krist., 79, 146, 1931.

moduli  $k_1$  and  $k_2$  corresponding to these may be very different, the behaviour of smectic substances results from this. In these,  $k_1$  is so much greater that the lengthwise distortion never occurs, and the axial lines are always straight lines. Hence follows the principle of the deformation of the smectic state, i.e., the conical structures which have been established by the beautiful work of G. Friedel. The law is obeyed perfectly by this whole range of complicated and remarkably interesting phenomena.

In nematic substances, on the other hand, the two moduli may be very nearly equal. Experiment shows that this may be true to a first approximation. Van Wyk 5 has worked out a theory for Case I that is almost identical with equation (2) given above. In his optical experiments, the great thickness of the layer used enabled him to put  $\phi_0 = 0$ . The observations are in good agreement with the theory. Further, Fréedericksz 6 has shown that his optical observations agree very well, both for Case I and Case II, with the theory which he adopted from van Wyk. In this, he does not assume that  $\phi_0 = 0$ , but applies the calculation to thin layers by the introduction of the elliptic function.

The difference between van Wyk's treatment and that given above will not be considered here. A practical application of Fréedericksz's measurements will, however, be made. It appears that for any given field strength there is a certain thickness of layer above which distortion first occurs. For less than this thickness, the distortion is zero, that is, any distortion would require a bigger expenditure of mechanical energy than would be available from the magnetic energy released by orientation in the field. The phenomenon is closely analogous to the behaviour of a loaded column, which only bends sideways at a fixed "breaking stress."

In equation (4) this implies that  $\phi_0 = \frac{\pi}{2}$ , and hence

$$\frac{z}{2}H\sqrt{\frac{\kappa_1-\kappa_2}{k}}=\int_0^{\frac{\pi}{2}}d\psi=\frac{\pi}{2}.$$

Fréedericksz showed that the product of  $z_0$  and  $H_0$  as given by this relation is constant; for p-azoxyanisole below 120° it has the value 8.4. From this,

$$z_0 H_0 = \frac{\pi}{\sqrt{\frac{\kappa_1 - \kappa_2}{k}}} = 8.4,$$

$$\sqrt{\frac{\kappa_1 - \kappa_2}{k}} = .37.$$

and therefore

From the measurements of Foex and Royer,  $\kappa_1 - \kappa_2$  is about 0.15  $\times$  10<sup>-6</sup>. Thus k must be  $1.0 \times 10^{-6}$  dynes.

For these very small magnitudes of the elasticity, it is obvious that, as Mauguin 4 has observed, it is not possible to obtain thicker layers in an unbent state without magnetic field. It is only possible to do so up to a thickness of 0.2 mm. Then, according to the above, a turningmoment of 10 - 4 ergs per cm.2 suffices to give the middle of the layer an angular distortion of unity. A torque of this magnitude might easily be introduced by differences in density caused by small temperature changes. Since the friction depends on the direction, heat convection can give distortions. The thicker the layer, the greater the difficulty with which a homogeneous orientation is achieved.

It is of interest to consider the highest torque per unit area of surface that can be achieved with the strongest available fields. This, of course, occurs at the outside of a thick layer, where it has the value

$$k\frac{d\phi}{dx} = H\sqrt{k(\kappa_1 - \kappa_2)}.$$

For 25,000 Gauss it gives, in the example just mentioned, 0.0004 ergs per cm.<sup>2</sup> The dimensions are those of a surface tension, the magnitude with which it competes. The orientation of the phase at the fixed plate is determined by the difference of surface tensions in the different positions. When the axes are parallel to the wall, the surface tension  $(\sigma_1)$  may be quite different from that when they are perpendicular  $(\sigma_2)$ , since the two surfaces actually possess quite different structures. The difference may be of the order of magnitude of 10 ergs per cm.<sup>2</sup>, which is 1000 times greater than the greatest attainable torque. This explains the fact observed by van Wyk and by Fréedericksz, that the angle at the surface against glass is independent of the field strength. If the surface tension is given by the relation

$$\sigma = \sigma_1 \sin^2 \phi + \sigma_2 \cos^2 \phi,$$

where  $\phi$  is the angle between the axis and the normal to the plate, then for  $\sigma_1 - \sigma_2 = 10$  ergs per cm.<sup>2</sup>, the change of angle would only be about two minutes.

The effect of the field on the capacity of a condenser filled with a nematic substance will next be considered. It will be assumed that we are dealing with Case I, and that the normal to the condenser plates makes an angle  $\alpha$  with the lines of magnetic force. The axial lines will then only lie in a plane if the direction of the axes at the surface lies in the same plane as the lines of electric and magnetic force. This case will be dealt with first in what follows. Let the angle between the direction of the axes and the magnetic field be  $\phi$ , that between the axes and the lines of electric force  $\chi = \phi + \alpha$ . The equation is the same as before (equation 4), except that  $\phi$  at the solid boundary has the value

$$\frac{\pi}{2}$$
 —  $\alpha$  instead of  $\frac{\pi}{2}$ . Then

$$\frac{z}{2}H\sqrt{\frac{\kappa_1-\kappa_2}{k}} = \int_{\phi_0}^{\frac{\pi}{2}-\alpha} \frac{d\phi}{\sqrt{\sin^2\phi - \sin^2\phi_0}}$$

$$= \int_{\psi_0}^{\frac{\pi}{2}} \frac{d\psi}{\sqrt{1-\cos^2\phi_0\sin^2\psi}}$$

$$= F(\cos\phi_0, \pi/2) - F(\cos\phi_0, \psi),$$

$$\sin\psi_0 = \frac{\sin\alpha}{2}$$

where

$$\sin \psi_0 = \frac{\sin \alpha}{\cos \phi_0}.$$

The numerical values of the two elliptic integrals of the first class, F, may be found from the tables. The dielectric constant  $\epsilon$  of the nematic layer in the field varies continuously from place to place in the condenser along the x-direction:

$$\epsilon = \epsilon_1 \cos^2 \chi + \epsilon_2 \sin^2 \chi$$

<sup>&</sup>lt;sup>9</sup> E.g. E. Jahnke and F. Emde, Funktionstafeln, Teubner, Berlin, 1928; L. Kiepert, Integralrechnung, Hanover, 1910.

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where  $\epsilon_1$  and  $\epsilon_2$  are the dielectric constants parallel and perpendicular to the axis respectively. If the change of capacity with field strength is attributed to an alteration of "the" dielectric constant, the quantity so obtained is an average value  $\epsilon'$ . This can be calculated from the "air distance" of the condenser plates, *i.e.*, the distance between the plates for which the capacity in air (or more accurately in vacuo) would be the same. The "air thickness" of the nematic layer is

$$\frac{z}{\epsilon'} = 2 \int_0^{z} \frac{dx}{\epsilon_1 \cos^2 \chi + \epsilon_2 \sin^2 \chi}.$$

Let  $\epsilon_2 - \epsilon_1 = \Delta$ . Then for zero field strength, the "air distance" is  $z/\epsilon_2$ , and for infinite

field strength,  $\frac{z}{\epsilon_2 - \Delta \cos^2 \alpha}$ . The difference

$$\frac{z}{\epsilon_2 - \Delta \cos^2 \alpha} - \frac{z}{\epsilon'}$$

can be put equal to

$$(\epsilon_2 - \epsilon' - \Delta \cos^2 \alpha) z / \epsilon^2$$

if  $\Delta$  is small compared with  $\epsilon_1$  and  $\epsilon_2$ . From the measurements of Jezewski 7 in the example taken above,  $\epsilon_2=5\cdot31$ ,  $\epsilon_1=5\cdot15$ , so that the above gives a good approximation. Hence

$$\epsilon' - \epsilon_2 + \Delta \cos^2 \alpha = \frac{2\epsilon^2}{z} \int_0^z \left( \frac{1}{\epsilon_2 - \Delta \cos^2 \alpha} - \frac{1}{\epsilon_2 - \Delta \cos^2 \chi} \right) dx$$

$$= \frac{2\Delta}{z} \int_0^z (\cos^2 \alpha - \cos^2 \chi) dx.$$
Putting (eq. 2)
$$dx = \frac{d\phi}{H\sqrt{\frac{\kappa_1 - \kappa_2}{k}(\sin^2 \phi - \sin^2 \phi_0)}},$$

and

$$\chi = \phi + \alpha$$

we obtain finally

$$\epsilon_{2} - \epsilon' = \Delta \left[ \cos^{2} \alpha - \frac{\{E(\cos \phi_{0}, \pi/2) - E(\cos \phi_{0}, \psi_{0})\} \cos 2\alpha + \cos \phi_{0} \cos \psi_{0} \sin 2\alpha}{F(\cos \phi_{0}, \pi/2) - F(\cos \phi_{0}, \psi_{0})} \right]$$
(5)

Here E is the elliptic integral of the second kind,

$$E(\cos\phi_0, \pi/2) - E(\cos\phi_0, \psi_0) = \int_{\psi_0}^{\frac{\pi}{2}} \sqrt{1 - \cos^2\phi_0 \sin^2\psi} \, d\psi.$$

It may be found in the tables.

This equation will be briefly discussed. Fig. 2 represents graphically the relation between  $\frac{\epsilon_2 - \epsilon'}{\Delta}$  and  $\frac{2}{zH\sqrt{\frac{\kappa_1 - \kappa_2}{k}}}$  for several values of  $\alpha$ .

When  $\alpha=0$ , the quotient in the bracket becomes  $\frac{E}{K}$ ; this expression was derived by Fréedericksz for the double refraction in Case I, and  $\mathbf{I}-\frac{E}{K}$ 

in Case II. This can easily be understood, because the double refraction, like the difference of the dielectric constants, is proportional to  $\sin^2 \chi$ . The axial lines in Figs. 1a and 1b have been drawn for Case I and Case II

when  $\alpha = 0$  and  $\phi = 20^{\circ}$ . It is interesting this formula that for  $\alpha \neq 0$ the discontinuous character of function disappears;  $\phi_0$ reaches value  $\frac{\pi}{2} - \alpha$  at the thinnest layer has a distortion, which, however, is very small for values of z below  $z_0$ . The effect is therefore not essentially different for values of  $\alpha$  of a few degrees; the function here shows a strong

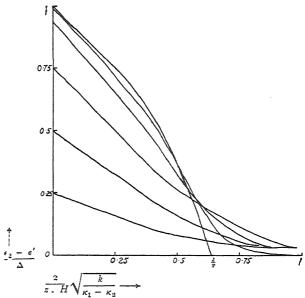


Fig. 2.—Graphs of 
$$\frac{\epsilon_3 - \epsilon'}{\Delta}$$
 plotted against  $\frac{2}{zH}\sqrt{\frac{k}{\kappa_1 - \kappa_2}}$  for  $\alpha = 0^\circ$ , 5°, arc  $\sin\frac{1}{4}$ , 30°, 45° and 60°.

curvature. (See the curve for  $\alpha=5^\circ$  in Fig. 2.) For large values of H the equation becomes

$$\epsilon_2 - \epsilon' = \Delta \left( \cos^2 \alpha - 2 \frac{\cos 2\alpha + \sin \alpha}{zH \sqrt{\frac{\kappa_1 - \kappa_2}{k}}} \right).$$

If the values of  $\epsilon_2 - \epsilon'$  are plotted against the reciprocal of the field strength, then at high field strengths straight lines are obtained which cut off an intercept on the y-axis proportional to  $\cos^2\alpha$ . Their slope is proportional to  $(\cos 2\alpha + \sin \alpha)$ , which has a maximum at  $\sin \alpha = 0.25$  ( $\alpha = 14^{\circ}29'$  approx.). For  $\alpha = 30^{\circ}$  the line is parallel to that for  $\alpha = 0$ , and becomes continuously less steep as  $\alpha$  increases. The curve for  $\alpha = 0$  is everywhere concave to the x-axis, but the other curves for small field strengths show a convex curvature towards it which is predominant above  $\alpha = 30^{\circ}$ . It is also of interest that the effect of the field strength in the neighbourhood of

$$H_0 = \frac{\pi}{z\sqrt{\frac{\kappa_1 - \kappa_2}{k}}}.$$

at first increases with increasing  $\alpha$ , and later decreases.

The measurements of Kast <sup>10</sup> and Jezewski (*loc. cit.*) may be adduced in support of the theory. In Fig. 3, curve (I) shows Kast's measurements I on p-azoxyanisole at II9° C. plotted against  $\frac{1}{H}$ , and curves (2) and (3) similar measurements for p-azoxyphenetole at I38° C. and I53° C. respectively. For large field strengths they are very nearly straight lines. It is not possible to calculate the curve a priori, as the thickness of the layer in the condenser is not given. But we can assume the value of  $\sqrt{\frac{\kappa_1 - \kappa_2}{k}}$  from the measurements of Fréedericksz, <sup>6</sup> and calculate the thickness from this:

$$z = \frac{2}{H\sqrt{\frac{\kappa_1 - \kappa_2}{k} \left(1 - \frac{\epsilon_2 - \epsilon'}{\Delta}\right)}}.$$

From the value for p-azoxyanisole at 119° C., for which

$$\sqrt{\frac{\kappa_1-\kappa_2}{k}}=\frac{\pi}{8\cdot 4},$$

z is found to be approximately 0.05 mm.; from p-azoxyphenetole at 153° C.,

$$\sqrt{\frac{\kappa_1 - \kappa_2}{k}} = \frac{\pi}{8.06},$$

and hence z is 0.03 mm. Curves (4) and (5) give the measurements of Jezewski for p-azoxyphenetole at 143° C. and p-azoxyanisole at 122° C. The curves appear to be irregular. The thickness z being given as 0.07 cm., the value of  $\sqrt{\frac{\kappa_1 - \kappa_2}{k}}$  calculated from the approximate course of

curve (4) is about half as big as that found from Fréedericksz's values of

 $z_0H_0$ , while from curve (5) it is about equal to it.

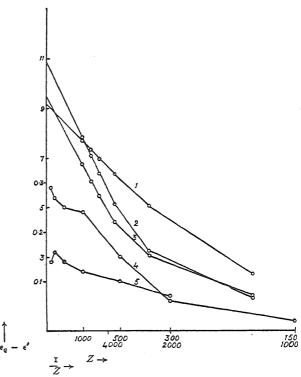
For small field strengths, however, Kast's measurements deviate considerably from the theoretical curve. His curves are convex instead of concave to the axis. Apart from the fact that the theory involves several doubtful assumptions, this discrepancy is not surprising. In the first place, the measurements are made with a condenser surrounded with nickel wire, so that the field strength, and field direction, must differ appreciably from that in the absence of nickel. Secondly, the theory only refers to that part of the condenser where the axis of the nematic substance is parallel to the condenser plate. But near the edge this is certainly not true. Further, dust particles (particles of the mica used for insulation) may cause deformation in the absence of a field. It has been shown that the effect is greatest when the angle between the axis and the magnetic field has an intermediate value, and the field strength is small.

The measurements II of Kast  $^{11}$  for varying angle  $\alpha$  will next be compared with the theory. Unfortunately Kast gives no complete table of his numerical results, so that the points in question have had to be taken from Figs. 3 and 4 of Kast's paper. Table I gives the change of acoustic

L. S. Ornstein, Ann. Physik, 74, 445, 1924.
 W. Kast, Ann. Physik, 83, 391, 1927.

interference frequency thus obtained; in this, the values taken from

Kast's Fig. 3 for  $\alpha = 0$  have been decreased by I per cent. to correct for the temperature difference 0.5° C. All the measurements lie in a range where  $\epsilon_2 - \epsilon'$ decreases lineally with the reciprocal of the field strength. In Fig. 4 are shown the corresponding straight lines calculated the actual distance between the plates of 0.75 mm. It is clear that the measured results agree well with those calculated. This is only one parameter  $\Delta$  was to be derived from the measure-



the more note- Fig. 3.—1, 2, 3. Measurements I of Kast.  $\epsilon_2 - \epsilon'$  in arbitrary worthy, that units (right-hand numbers along y-axis), H in gauss (upper numbers along x-axis).

meter A was to 4, 5. Measurements of Jezewski.  $\epsilon_2 - \epsilon'$  in absolute units (left-

hand numbers along y-axis), H in gauss (lower numbers along x-axis).

ments; and incidentally, the straight lines here obtained could have been arrived at beforehand, using only the optical measurements of Fréedericksz. The swarm theory introduces a second parameter,

$$x = \frac{\kappa_1 - \kappa_2}{kT} v,$$

TABLE I.—Change of Acoustic Interference Frequencies according to Kast, II.

μ α	2900 f. 0° 2250	725•	375-	225.
o° 25° 35° 45° 60° 70°	537 432 348 276 165 96	494 391 318 251 124	357 289 — — 72	377 262 184 — 68 51

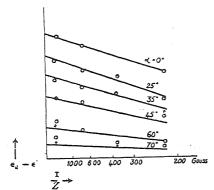
besides that mentioned above; it is to be noted that this second parameter is about twenty times bigger when calculated from measurements II than when calculated from measurements I. It is easy to see that this depends on the layer thickness, which is twenty times as great in II. A systematic deviation is only shown by the values for  $\alpha = 70^{\circ}$ , which are greater than were to be expected. This is evidently connected with the fact that a change of acoustic frequency is observed even for  $\alpha = 90^{\circ}$ , which is not easy to account for. It would seem reasonable to subtract this value for  $\alpha = 90^{\circ}$  from all the other values, when good agreement is obtained even for  $\alpha = 70^{\circ}$ . According to Jezewski, the values for the greatest field strengths are represented very accurately by the formula

$$\epsilon = \epsilon_1 \cos^2 \alpha + \epsilon_2 \sin^2 \alpha$$
.

The way in which the effect depends on temperature is of particular interest. According to Ornstein, the change in dielectric constant can be written

$$f(H) \cdot g(T)$$
.

This can only be correct to a first approximation; only, in fact, if the



calculated values.

variation of  $\Delta$  with the temperature is appreciable, while that of  $\frac{\kappa_1 - \kappa_2}{L}$  is negligible. According to the experimental results of Fréedericksz,  $z_0H_0$  decreases with rise of temperature, and therefore  $\frac{\kappa_1 - \kappa_2}{L}$  increases with rise of temperature. This means that for increasing temperature k decreases more rapidly than  $\kappa_1 - \kappa_2$ . Hence  $\frac{\epsilon_2-\epsilon'}{\Delta}$  is reached with smaller

4.—Measurements II of Kast. field strengths as the temperature Graph of  $\epsilon_2 - \epsilon'$  plotted against  $1/\zeta$ . rises.  $\kappa_1 - \kappa_2$  should to a first The straight lines represent the approximation decrease in the approximation decrease in the same way with rising temperature

as do  $\Delta$  and the double refraction  $n_1-n_2$ . Even at the temperature of transition into the amorphous phase, the various kinds of anisotropy possess values different from zero. From the variation of k with temperature follows, according to the Second Heat Theorem, that a change of deformation with change of temperature is connected (cooling associated with deformation, heating with release from deforming forces). The very small size of the effect (order of magnitude  $10^{-50}$ ) makes proof scarcely possible. Moll and Ornstein 12 observed such an effect, but it was of the opposite sign. For Case III no change of temperature was observed, though the order of magnitude of that expected was the same. The observation that was made must be due to some other effect.

#### Experimental Section.

Our experiments on the magnetic behaviour of nematic layers relate to two different problems. Till now no exception had been found to the rule that optic axes tend to set parallel to the lines of magnetic force; in other words, that the susceptibility along the axis is greater (the diamagnetism smaller) than at right angles to it:

$$\kappa_1 - \kappa_2 > 0.$$

We now tried to see if substances of quite different constitution from those hitherto examined might not furnish examples of the opposite behaviour. With this in view, we investigated a number of aqueous nematic systems. The experiments showed that nematic concentrated solutions of bromo-phenanthrene sulphonic acid and chlorophenanthrene sulphonic acid, which showed large effects in a magnetic field, both set with their principal axes perpendicular to the lines of force. Since both these systems have negative double refraction, the vibration corresponding to the greater refractive index here lies parallel to the lines of force, just as in the substances previously examined. But the law, even as thus stated, is not generally valid. Thus a concentrated solution of salvarsan is definitely affected by a magnetic field, though to a smaller degree, and sets with the direction of its axis perpendicular to the lines of force. Its double refraction is positive, and hence the vibration direction of greater refractive index is perpendicular to the lines of force. On the other hand, the phase which occurs in a moderately concentrated aqueous solution of potassium laurate seems to show a tendency to set with its axis parallel to the lines of force. Its double refraction is negative, like that of the halogen phenanthrene sulphonic acids, so that in this, as in salvarsan, the vibration direction of greater refractive index is perpendicular to the lines of force.

These experiments show that the rule that the axes tend to set parallel to the lines of force does not always hold.

The rest of our work involves the actual performance of the experiments described as Case III in the theoretical part of the paper. They are purely qualitative, and only give a preliminary account of the orientation. It was necessary for these experiments to obtain preparations with the greatest possible uniformity of orientation of their axes parallel to the surface (which was of glass). For this purpose, we made use of the effect on the orientation of the nematic phase produced by rubbing the glass surface. 13 If a glass plate is rubbed in a given direction, then the nematic phase in contact with it sets with its symmetry axis parallel to the direction of rubbing. The substances to be investigated, p-azoxyanisole and anisaldazine, were placed between a plane glass plate and a plano-convex lens, the adjoining surfaces of which were rubbed in the same direction by means of a rotating leather pad. (Layers between a lens and a plate have been used by Lehmann and also by Fréedericksz.) The orientation is almost perfect if the force used in polishing is sufficient. If the direction of rubbing on the plate and the lens are accurately the same, the substance appears dark between crossed nicols when the direction of one nicol is parallel to the direction of rubbing. It is in thicker layers that the well-known self-contained distortions about the lines of discontinuity mostly occur. The preparation was placed in a perforated copper block, electrically heated

<sup>&</sup>lt;sup>13</sup> H. Zocher and K. Coper, Z. physik. Chem., 132, 295, 1928.

above and below the magnetic field, in such a position that the direction of rubbing made only a very small angle with the normal to the lines of force. Observations were made with a polarising microscope. If the polarising prism was set in the extinction position for zero field strength, then when the field was put on the thicker layers became brighter. Near the point of contact of lens and plate, out to a fixed radius from the centre, no effect occurred. (See photograph, \* Fig. 5.) This phenomenon is completely analogous to that observed by Fréedericksz for Cases I and II. The values of  $z_0H_0$  are of the same order of magnitude as his, and hence  $k_t$  is also of the same order of magnitude as  $k_1$  and  $k_2$ . In the part where the effect occurs, the optical behaviour of the layer is of a rather complicated nature. If white light is used, the thicker layers show high order white. The actual tint, however, is not the same as for zero field, but is brownish. This was to be expected. Mauguin 14 showed that for a system in which one surface is rotated relative to the other, a vibration which is initially parallel to the first layer only changes its direction, and emerges parallel to the second layer, so long as the rotation effect is small compared with the double refraction. Hence in the above case, since the first and second layers are parallel, no change would be observed if the ratio of the rotation effect to the double refraction were small. Differences are only observed when this condition is not fulfilled. But for red light the double refraction is very much smaller than for light of shorter wave-length. Therefore the effect must be much more marked in the long-wave part of the spectrum than in the short-wave region, and hence the emergent light must have a brownish tint.

Extinction cannot be obtained by turning the nicols, as in the case of an unrotated layer. If the nicols are respectively parallel and perpendicular to the direction of rubbing, and if a gypsum plate of first order red is introduced between the specimen and the analyser, at 45° to the vibration direction of the nicols, a change appears in the red interference colour which is superimposed on the rather dull high order white. The axial lines of the layer between the two plates must, of course, lie in the same pair of quadrants between the field direction and its normal as does the direction of rubbing. With the gypsum of first order red, a blue addition colour is then obtained if the vibration direction of greater refractive index of the gypsum lies in the other pair of quadrants; if it lies in the same pair of quadrants as the axial lines, a yellow subtraction colour results. The same effect could be brought about without the application of the field, by turning the preparation through a small angle in the pair of quadrants containing the axial lines, and at the same time introducing between the preparation and the gypsum a thin flake of a substance of weak double refraction, with its vibration direction of greater refractive index at about 45° in the second pair of quadrants. The layer rotated in a non-uniform manner by the field therefore produces on the plane-polarised light from the polariser an effect which is to a first approximation the same as that of a layer of high order white on which is superimposed a weakly doubly-refracting layer of constant thickness and different orientation.

The observations in monochromatic light agree with these results. In sodium light, in the absence of a magnetic field, the field of the microscope is dark; but when a magnetic field is applied, it shows a large

number of interference rings in the parts where the thickness is great. These cannot be made to disappear by turning the polariser. But if a thin flake of mica (for example, a quarter-wave plate) is introduced between analyser and specimen, then by turning the flake and the analyser a position can always be reached in which the fringes vanish in a region covering a large number of rings (from 5 to 10). In this region there is uniform illumination which varies as the polariser is rotated. The vibration direction of the mica with the greater refractive index is here only turned through a small angle from the direction of rubbing in the quadrants containing the axial lines. The thicker the layer and the stronger the magnetic field, the greater must this angle be. For a given field-strength, the interference fringes in a fixed zone can be made to disappear without turning the analyser, by turning the mica Then zones nearer the centre, where the layers are thinner, require the analyser to be turned in the same direction as the mica, those further from the centre in the opposite direction. This shows that for increasing thickness of the layer, as for increasing magnetic field, the double refraction of the imaginary flake of constant thickness must be increased. No appreciable displacement of the interference rings depending on the field strength was observed, which means that the double refraction of the layer of variable thickness (high order white) did not alter appreci-The azimuth of this can be determined by turning the polariser into the position where the uniform illumination is of minimum intensity. The greater the field strength and the thickness of the layer, the more does it differ from the direction of rubbing. On removal of the mica, the fringes in this position reappear, though they are of small intensity. This implies that the model assumed does not correspond accurately to the properties of the layer.

More accurate observation shows that the position of the axis at the surface is not absolutely independent of the field strength. The difference between the surface tensions when the axes are parallel and perpendicular to the direction of rubbing depends on the anisotropy of the glass surface, and will not necessarily be of the same order of magnitude

as the difference previously referred to between  $\sigma_1$  and  $\sigma_2$ .

Finally, another experimental possibility should be mentioned which does not correspond to any of the three Cases I, II, or III, and which we have been able to realise in practice. In this, the assumption is no longer made that the orientation at the two surfaces is the same. For example, if one of the glass surfaces is treated with acid, p-azoxyanisole tends to set with its axis perpendicular to the surface. Hence in this case the axes at one surface are parallel to the direction of rubbing, and at the other they are perpendicular to the surface, and so a distortion occurs when no field is present. This will be constant throughout the layer,

$$\frac{d\phi}{dx} = \frac{\pi/2}{2}$$
.

Calculation shows that the phase-difference due to the double refraction is half as great as when the axes at both surfaces are parallel to the direction of rubbing. The experiments confirm this result, at least to a first approximation. A magnetic field acting parallel to the surface then brings about a large decrease in the diameter of the interference rings, that is, an increase in the path difference, which becomes almost double its previous value.

# MAGNETIC PROPERTIES OF MESOMORPHIC SUBSTANCES. ANALOGIES WITH FERROMAGNETICS.

By G. Föex (Strasbourg).

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Mesomorphic bodies are organic compounds, which, like all substances of this nature, are diamagnetic; that is to say, their susceptibility is very feeble and negative. When placed in a strong non-homogeneous field, they suffer slight repulsion. For the compounds studied, the mass-susceptibility, or coefficient of magnetisation, measured on the powdered solid, has a value which can be calculated on Pascal's additivity law. The magnetic properties are perfectly normal, which is enough to invalidate the theories which attribute the orientation by the field to the existence of a magnetic moment within the molecule.

#### 1. Nematic Substances.

# Spontaneous Orientation, and Mechanism of Orientation by the Field.

Nematic substances are always and spontaneously bi-refringent, and uni-axial. In the absence of any external directing action, the orientation of the optic axis taken at random varies from point to point; the substance, which always has a thread-like texture, appears cloudy if sufficiently thick.

Mauguin <sup>2</sup> has shown that, in a magnetic field of sufficient intensity, the optic axis sets itself parallel to the lines of force. If the field is uniform, the substance assumes, in all its parts, the optical properties of a uni-axial crystal, the axis of which would be parallel to the field.

To explain these properties, it is assumed that the molecules—which are very long and comparable with needles—set themselves parallel to their length, according to their mutual reactions.

In a very small element of volume, containing nevertheless a large number of molecules, the axes are nearly parallel: in the absence of external action their direction is fortuitous; it varies probably progressively, from one element of volume to another and is a function of the times for each element.

A sufficiently intense magnetic field brings about the same directive effect upon all the elements of volume of which the substance is composed. The axes are orientated spontaneously: the direction is determined by the field. The large size of the molecules, consisting of a nearly straight chain of atoms, causes them to be arranged along the lines of force. This behaviour appears from the study of the optical properties, and especially from Kast's work, by means of X-rays, upon the nematic state in azoxyanisol when orientated by a field.

<sup>&</sup>lt;sup>1</sup> E.g. that of L.[S. Ornstein, Ann. Physik., 74, 445, 1924. <sup>2</sup> C.R., 152, 1680, 1911. 

<sup>3</sup> Ann. Physik, 83, 418, 1927.

From the uni-axial nature of these bodies, it appears probable that the molecules are orientated at random about their axis. The study of diamagnetism in an orientated crystal shows that, in all probability, the molecules have no axial symmetry.

The orientation by the field results from the magnetic anisotropy of the molecules, and the direction along which the diamagnetism is least tends to be parallel to the field. In isotropic liquids the molecular orientation by the field always remains very small, and produces magnetic birefringence. In the nematic stasis, orientation is spontaneous, and the minute directive action exerted by the field on diamagnetic anisotropic molecules suffices to impose on the axes the field-direction throughout the bulk of the specimen, with the exception perhaps of the immediate neighbourhood of the walls.

#### Orientation as a Function of the Field.

In thin layers contained between glass plates, the action of the field is impeded by the directive action of the walls. Thus, with a thickness of 0.01 mm., the faces being parallel to the lines of force, Mauguin has observed a continuous increase in birefringence, with a field up to 7000 Gauss; at this intensity the limit was still not attained. With a thicker layer, arranged as before, the birefringence increased up to 5000 Gauss, and then remained practically constant between that figure and 7000 Gauss, at which saturation was attained. The curves published by Freedericksz and Repiewa 4 show that, for a given field, the birefringence increases very rapidly with the thickness of the layer, at least up to 0.15 mm.

To Van Wyck  $^5$  we owe an important study of orientation by a field in layers of para-azoxianisol, having a thickness of I to 2 mm. The central part was easily orientated, but in the superficial layers, very near the glass, the molecules, being subject to two directing forces at once, were not completely orientated. Van Wyck deduces from his data that the thickness of the superficial layer in which the molecules do not have their axes parallel to the lines of force, varies inversely as the field. This thickness is of the order of 0.01 mm. for H=1260 Gauss, and of the order of 0.002 mm. for H=10,000 Gauss.

Kast <sup>6</sup> has studied the specific inductive capacity in the mesomorphic state, with the magnetic field perpendicular to the plates of the condenser used in the experiments. The orientation produced by the field diminishes the specific inductive capacity. The isothermals obtained, representing the latter as a function of the field, have the same character as those giving the relationship between field and magnetisation of a ferromagnetic substance (Figs. I and 2).

The orientation is already nearly complete in a field of 1000 Gauss, but continues, however, to increase slightly up to the limit of the field attained. The thickness of the slice not being given, it is difficult to know whether the slow increase of the orientation in fields higher than 1000 Gauss affects entirely the superficial layers, or whether an effect on the whole substance arises.

The information which we actually possess is altogether insufficient to determine the law of increase of orientation as a function of the field in the interior of a thick layer of liquid, in a region where the influence

<sup>&</sup>lt;sup>4</sup> Z. Physik, 42, 532, 1927.
<sup>5</sup> Ann. Physik, V, 3, 879, 1929.
<sup>6</sup> Ann. Physik, IV, 73, 145, 1924; and Z. Physik, 42, 81, 1927.

of the vessel no longer makes itself felt. In particular, we do not know whether the field only plays a part in rendering uniform the direction of the spontaneous orientation in the whole substance, or whether, on the contrary, it causes the orientation to increase above the limit which it reaches spontaneously.

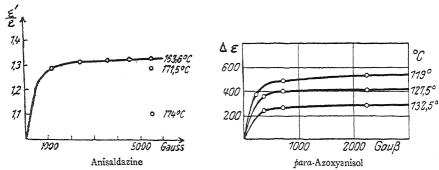


Fig. 1.—Variation in the specific inductive power (absolute values) of anisald-azine and p-azoxyanisol as a function of the field, according to Kast (arbitrary units).

Experiments upon the law of orientation as a function of the field remain to be made. It would be easy to carry out such work by making observations upon the magnetic susceptibility in different fields on a considerable volume of a mesomorphic substance.

# Magnetic Susceptibility.7

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Solid Para-azoxyanisol.—The powdered solid, formed of a large number of crystalline fragments orientated in all directions is isotropic by com-

pensation. Its diamagnetism, which is independent of the temperature, is given by

$$x = -5.65 \times 10^{-7}$$
.

This compound crystallises in the monoclinic system: the crystal possesses the following elements of symmetry, a diad axis, a plan perpendicular to it, and a centre. Of the three principal directions, one is of necessity directed along the axis, the other two lie in the plane of symmetry. Measurements have shown that these two directions make an angle very close to 45° with the axis OX of the plane of symmetry. The principal coefficients have the following values, per unit mass:

Fig. 2.—Position of the magnetic axes in the plane of symmetry.

$$\chi_1 = -6.65 \cdot 10^{-7}$$
 $\chi_2 = -6.34 \cdot 10^{-7}$ 
 $\chi_3 = -4.08 \cdot 10^{-7}$ 

and referred to molecular weight:

$$\chi_1 = -172 \cdot 10^{-6}$$
 $\chi_2 = -164 \cdot 10^{-6}$ 
 $\chi_3 = -105 \cdot 10^{-6}$ 

<sup>7</sup> G. Föex, J. Physique, VI, 10, 421, 1929.

The variations of diamagnetism with direction arise on the one hand from the anisotropic character of the molecules, and on the other hand from their orientation. The anisotropy of para-azoxyanisol is not exceptionally large; it is less than that of several substances which do not occur in the mesomorphic stasis, for example,

Naphthalene,8 with molecular coefficients,

$$-70, -42, -154,$$

Hexamethylbenzene, with molecular coefficients,

$$-105, -116, -190,$$

Benzene, anthracene, etc.

For these substances in the liquid state, molecular orientation by a magnetic field always remains very small, as is demonstrated by the study of magnetic birefringence, which points to the absence of mutual actions akin to those which produce spontaneous orientation in nematic bodies.

In para-azoxyanisol (crystal) the principal coefficients of magnetisation vary very little with the temperature. Thus  $\chi_3$  varies at least I per cent. in relative value between — 80° and + 15°. This shows that thermal agitation has little effect upon the orientation of the molecules in the crystal.

#### The Nematic Stasis.

An anisotropic diamagnetic sphere, free to set itself in a magnetic field, takes up a position such that its direction of minimum diamagnetism coincides with that of the field. A needle, cut out of an isotropic diamagnetic substance, sets perpendicular to the field.

In nematic bodies the greatest dimension of the molecules is along the lines of force, which shows that this greatest dimension is a direction of minimum diamagnetism, and that the minimum should be well marked. It follows that if the molecular properties remain unchanged, the diamagnetism should be more feeble in the orientated nematic statis than in a powdered solid or in an isotropic liquid.

Again, since the orientation decreases as the temperature rises, it may be inferred that the coefficient of magnetisation, instead of remaining independent of temperature as in ordinary substances, increases in absolute value with the temperature, and tends towards the value which it possesses for the liquid.

Observations have completely justified these anticipations and consequently a new confirmation of our ideas on the subject of the nematic stasis has been obtained.

Fig. 3 represents the variations of the absolute value of  $\chi$  for para-azoxyanisol as a function of the temperature for a field of some 8000 Gauss.

Below II6° the substance is a crystalline powder, almost isotropic by compensation and with constant diamagnetism. At II6° fusion sets in; the nematic phase already formed is orientated by the field,  $\chi$  changes (at constant temperature) from  $-5.52 \times 10^{-7}$  to  $-4.57 \times 10^{-7}$ . Immediately the diamagnetism increases, at first fairly rapidly, and then towards I33° discontinuously. Below I33° the substance is an isotropic liquid, and the value of  $\chi$  remains close to  $-5.45 \times 10^{-7}$ .

On super-cooling, it is possible to extend the domain of the existence

<sup>8</sup> Bhagavantam, Proc. Roy. Soc., 124, 545, 1929, and 126, 143, 1929.

of the nematic phase to 90°. At the moment of crystallisation the coefficient of magnetisation returns sharply to the value —  $5.65 \times 10^{-7}$  which it had in the solid, or to a value slightly different if the crystallisation, in favouring certain directions, does not yield an isotropic solid on the average.

Azoxyphenetol, azoxyanisolphenetol and anisaldazine give analogous results.

If the coefficient of magnetisation of the isotropic liquid is called  $\chi_{is}$  and that of the orientated nematic phase  $\chi_{or}$ , the difference  $\chi_{is} - \chi_{or}$ 

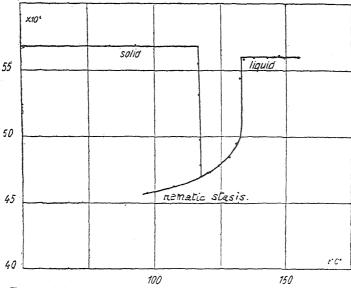


Fig. 3.—Diamagnetism of para-azoxyanisol at different temperatures.

varies in the same sense as the orientation of the collection of molecules. This difference increases when the temperature at which  $\chi_{or}$  is measured diminishes, since thermal agitation affects the orientation less. The greatest value for this difference is attained at the lowest temperature compatible with the existence of the nematic state, that is to say, in carrying the super-cooling as far as possible. The following values for this difference, referred to  $\chi_{is}$ , have been found for various substances:

Substance,			$\chi_{is} - \chi_{or}$	
<b>.</b>				$\chi_{is}$
Para azoxianisol .				0.193
Para azoxiphénétol .				0.173
Para azoxianisolphénétol				0.186
Anisaldazine				0.174

These figures are lower than those corresponding to complete alignment of the molecules, since thermal agitation tends to increase  $\chi_{or}$ 

For azoxyanisol the limiting value of  $\frac{\chi_{is} - \chi_{or}}{\chi_{is}}$  is furnished by the crystal, and amounts to approximately 0.283. The difference 0.283 - 0.93 = 0.09 shows the effect of thermal agitation at a temperature in the neighbourhood of 90° C. The number characteristic of the orientation is only two-thirds of that which it would be if thermal agitation did not exist.

G. FÖEX 963

# Comparison with Ferromagnetic Substances.

The magnetisation of iron and kindred substances is attributed to orientation of the atoms, or at least to orientation of their magnetic axes along the field. Orientation, which must be very complete at saturation, presents an evident analogy with that of nematic molecules, as has been stressed by Bose 9 and many others. It becomes much more striking when it is recognised that in both cases orientation is spontaneous, and that the part played by the field is to render the direction of the axes uniform throughout the bulk of the substance.

#### Orientation as a Function of the Field.

These analogies are brought out by the curves which show the orientation of the molecules either as a function of the field or as a function of the temperature.

Kast's curves relating to the dielectric constant have a marked family likeness to the curves of magnetisation. In both instances, a rapid increase of orientation followed by a tendency to saturation may be perceived.

One must not press the analogy too far; the variations of the dielectric constant and magnetisation are really two phenomena which depend upon orientation but according to different laws.

# Orientation as a Function of the Temperature.

The difference  $\chi_{is} - \chi_{or}$  of the coefficients of magnetisation of an isotropic liquid and of the orientated nematic stasis varies in the same

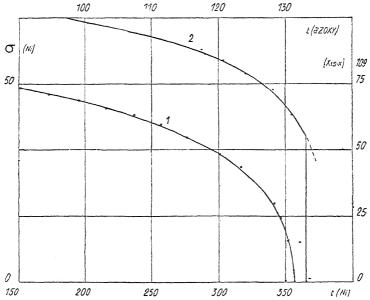


Fig. 4.—Curve 1: spontaneous magnetisation of nickel. Curve 2:  $\chi_{is} - \chi_{or}$  for para-azoxyanisol.

sense as the orientation of the molecules, and affords a certain measure of it. The curve which represents this difference as a function of the

<sup>9</sup> Physik. Z., 9, 708, 1908.

temperature has the same general appearance as the curve of spontaneous

magnetisation for nickel.

For both substances the orientation decreases as the temperature rises, first slowly, then more rapidly: for ferromagnetics it disappears without any discontinuity, at the Curie point. For azoxianisol, on the contrary, a discontinuity appears at 133°, i.e., at the clearing-point, and the orientations curve would, if prolonged, cut the temperature axis much further along.

The fact that the spontaneous orientation vanishes progressively for ferromagnetic substances whilst it disappears discontinuously for

nematic substances suggests the following question:

Do some other differences exist between the nematic stasis and an isotropic liquid besides molecular orientation in the former which might account for their discontinuity?

It is possible to imagine several: for example, the existence of crystalline elements <sup>10</sup> in the nematic stasis. At the clearing point, the destruction of these crystalline elements would produce the observed discontinuity. Or again, the molecules, rigid below the clearing-point, cease to be so above it (Friedel).<sup>11</sup>

These different hypotheses are not essential for interpreting the observed differences between ferromagnetics and nematics. Thus the size of the particle subject to orientation is by no means the same in the two cases: it may be perhaps simply an electron pivoting in ferromagnetics, but certainly a large molecule in mesomorphic materials. On the other hand, the spontaneous magnetisation and the difference  $\chi_{is} - \chi_{or}$  are associated with the orientation of the particles according to different laws. Magnetisation depends upon the cosine of the angle which the magnetic axis makes with the field, whereas  $\chi_{is} - \chi_{or}$  is a function of the square of the cosine.

# Magnetic Birefringence in Isotropic Liquids.

The spontaneous magnetisation of ferromagnetic has been attributed by P. Weiss to mutual interactions between magnetic atoms. Although spontaneous magnetisation disappears at the Curie point, these mutual interactions continue to make themselves felt above this temperature, thus favouring magnetisation. It follows that the coefficient of magnetisation, instead of being given by Curie's Law  $\chi = C/T$ , is given by

Weiss's law,  $\chi = \frac{C}{T-\theta}$ , where  $\theta$  represents the Curie point. The constant C is identical in both cases if it is assumed that the magnetic moment of the atom is the same.

For a ferromagnetic at a temperature above the Curie point, the magnetisation is greater than for an ordinary paramagnetic ( $\theta=0$ ), and it varies much more rapidly as a function of the temperature. The ratio of the coefficients of the two substances in question, at a temperature T is

$$\frac{\chi_{\text{ferro}}}{\chi_{\text{para}}} = \frac{T}{T - \theta}.$$

By analogy, one might thus consider that in a nematic substance above its clearing-point, the mutual effects between should again appear, and tend to establish orientation by the field. There should, therefore,

<sup>A. Cotton, Le Magnétisme, Rapports Conseil Solvay, p. 423, 1930.
Ann. Physique, ix, 18, 274, 1922.</sup> 

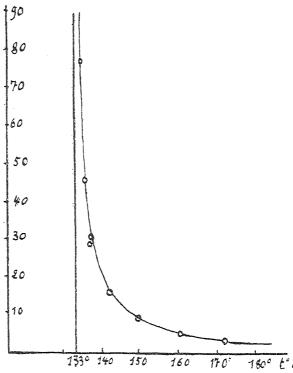
result a stronger magnetic birefringence than in ordinary liquids varying very rapidly with temperature.

It is just this which Mlle. Zadoc Kahn <sup>12</sup> has observed for paraazoxyanisol. At 1.4° above the clearing-point the magnetic birefringence is equal to 77.6 times that of nitrobenzene at 22.5°. It decreases hyperbolically as the temperature rises.

These facts are in complete accord with the predictions of the "molecular field" hypothesis. Cotton has given an alternative ex-

planation. He supposes that poly-molecular crystalline elements already exist in the crystal, subsisting in the mesomorphic stasis, where they would no longer be arranged according to a regular reticulated structure. These elements would not be fixed relative \$50 to each other, and would be capable of assuming identical orientations under the influence of the field.

The magnetic birefringence observed by Mlle. Zadoc Kahn could be explained on the assumption that certain of the crystalline blocks exist in the liquid in some proportion which varies with the temperature.



with the tempera- Fig. 5.—Magnetic birefringence of p-azoxyanisol. Thickness of liquid 20 mm. Field 33,900 Gauss.

The hypothesis just mentioned seems difficult to reconcile with the fact that a nematic substance and an isotropic liquid form two distinct stases (Friedel), separated by a transformation temperature, at which the properties vary discontinuously. Should these discontinuities be produced by fusion of the blocks, melting may be complete and no crystalline particle should remain in the isotropic liquid.

## The Thermomagnetic Effect. 13

When magnetisation of a ferromagnetic substance changes, a reversible liberation of heat occurs which thermodynamical reasoning permits one to anticipate. P. Weiss has calculated the magnitude of the effect in connection with his theory of the molecular field. The rise of temperature dt produced by an adiabatic increase in magnetisation is

<sup>&</sup>lt;sup>12</sup> C.R., **191**, 1002, 1930.

<sup>13</sup> P. Weiss, J. Physique, VI, I, 161, 1921.

proportional to the square of the latter quantity. Fig. 6 shows the results obtained by Weiss and Forrer for nickel. The temperatures of the metal at the moment of the experiment are plotted as abscissæ, whereas the ordinates are the variations in temperature produced when the magnetisation varies from zero to the value which corresponds to the field, and at the temperature in question.

In the immediate neighbourhood of the Curie point the rise of temperature considerably exceeds 1°. It decreases when the temperature is increased, and tends rapidly towards zero. This means that, in this region, the magnetisation is feeble, and drops quickly as the temperature rises.

Below the Curie point, the field produces two different effects:

(1) A change of orientation of the magnetisation;

(2) A change in its magnitude.

The former is not concerned with the liberation of heat; the latter alone is efficacious. At low temperatures the second effect, to all intents and purposes, does not exist. The substance possesses spontaneous magnetisation near to saturation, and fields, even if very strong.

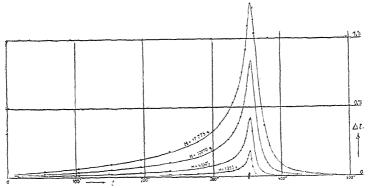


Fig. 6.—Thermo-magnetic phenomena at different temperatures.

are incapable of increasing the orientation. This accounts for the small scale of the thermomagnetic effect in this temperature region where the magnetisation is very intense.

In nematic materials one can foresee the existence of a phenomenon analogous to the thermomagnetic effect. This effect should vary in the same way as a function of the temperature, that is to say, it should have a very sharp maximum near the clearing-point. It is not impossible that with sufficiently strong fields observations might be made over this point.

The effect in question appears to have been brought to light by Moll and Ornstein, using a thermoelectric couple soldered to a thin silver plate immersed in para-azoxyanisol. When a magnetic field normal to the plate is switched on, a rise of temperature occurs. A complete study of the phenomenon, as a function of the field and of the temperature, would provide some interesting information: it would enable a distinction to be made between the fraction of the orientation which exists spontaneously, and that which is due to the field.

The comparison of the results found with those furnished by nickel allow a definite choice to be made between the hypothesis of molecular orientation and that of crystalline aggregates.

#### Conclusion.

A comparison between ferromagnetic and nematic substances has enabled several of the latter's properties to be anticipated: variations of diamagnetism with temperature; magnetic birefringence above the clearing-points; the probable existence of a thermo-magnetic effect. Characteristics which depend upon orientation are very similar for both kinds of materials. The result is that apart from the discontinuity of the orientation-temperature curve all the magnetic properties of the nematic stasis can be accounted for satisfactorily by means of the hypothesis of molecular-orientation.

#### 2. Smectic Substances.

On passing, by rise of temperature, from a solid which is isotropic by compensation to the smectic stasis, small and irregular variations in  $\chi$  are observed, but always an increase. These variations betray a feeble orientation of the whole; but this orientation has an accidental character, for it is not due to the field, since its direction appears to bear no relation to the latter.

For ethyl azoxibenzoate a magnetic field of 12,600 Gauss does not appreciably modify the structure and orientation acquired by the substance at the moment of fusion. If the field acts during fusion the same remarks apply.

On the other hand, if a field is present during the process of cooling of an isotropic liquid to the smectic stasis, orientation of the whole sets in, which is manifested by a strong decrease in diamagnetism.<sup>15</sup>

Fig. 7 shows the variation of  $\chi$  obtained under these conditions.<sup>7</sup>

The absence of an effect by a field when subjecting a solid to fusion is perhaps due to orientation of the smectic stasis by the crystals which give rise to it. The changes in  $\chi$  with temperature for smectic bodies are different from those characteristic of the nematic type. They are small and approximately linear, while the mesomorphic state persists, becoming very strong and discontinuous at the moment of passing into the isotropic state.

The discontinuity illustrates clearly the characters which should be associated with a transition of one phase to another:  $\chi$  increases in absolute value at constant temperature, according as the smectic stasis disappears. From this point of view the smectic state, as Friedel has maintained, is much more akin to the crystalline than the nematic: the discontinuity of the properties at the moment of passing over into the isotropic state is more marked.

Another difference from nematic bodies may be noticed, in that for them orientation takes place already under the influence of a field of several thousand Gauss, and if the field increases orientation does not become more complete to any appreciable extent: saturation is practically attained.

<sup>&</sup>lt;sup>15</sup> Orientation produced thus has been noticed by Freedericksz and Repiewa, loc. cit., 4.

For smectic substances complete orientation needs a much more intense field. For example, for ethyl para-azoxyanisol

н.	$\chi_{is} - \chi_{or}$		
11.	Xis		
6.500	0.112		
12.600	0.173		
18.500	0.183		

The limit reached, 0.183, has the same order of magnitude as for nematic materials (see p. 962), but it is much more difficult to attain.

It is possible to account for this difficulty which smectic specimens experience in orientation, by the tendency which their molecules possess to arrange themselves on parallel surfaces (focal conic structures or planar structures) with their optic axis normal to these surfaces.

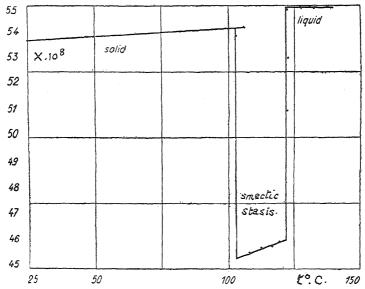


Fig. 7.—Variations of diamagnetism with temperature for ethyl para-azoxy-anisol.

Measurements by Freedericksz and Repiewa <sup>16</sup> show that the birefringence of thin orientated layers by the field is independent of thickness. Orientation is then homogeneous throughout the bulk of the section, including the superficial layers in contact with the glass.

## 3. Crystallisation in a Magnetic Field.

A. Nematic.—If melted azoxyanisol is allowed to crystallise in a cylinder I cm. in diameter, placed axially in a magnetic field, Kast <sup>17</sup> has obtained a solid formed of small crystals all of which are arranged in the same direction. In the solid the axis of the molecules was, as in the nematic stasis, parallel to the field. This structure was determined by means of X-ray analysis. Either a directive action of the field on the crystals during formation may be supposed, or an orientation of the

<sup>16</sup> Z. Physik, 42, 546, 1927.

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crystals by the nematic stasis. G. Friedel has mentioned several examples of these orientations of one stasis by the other.

A study of the same question, using the diamagnetism as a criterion of the orientation, has led the present author independently to results

altogether in agreement with those of Kast.

The substance, in a cylindrical container, 8 mm. diameter, with the axis vertical, is placed, during crystallisation, in an intense horizontal magnetic field. If crystallisation occurs at the limit of surfusion and is very rapid, the crystals are very little, or even not in the least, orientated. The coefficient of magnetisation rises sharply from the small value which is assumed when the molecules are orientated, to the much higher value belonging to the isotropic solid.

One obtains, on the contrary, orientated crystals by the following method—the solid is carefully melted in the magnetic field, the heat is moderated when no small fragment of the solid remains, then slow

cooling is permitted so as to produce crystallisation.

The coefficient of magnetisation, observed during the course of this operation, maintains a strictly constant value from the moment at which cooling begins. This value corresponds to that of an orientated nematic substance at the temperature of solidification. The orientation of the molecules in the solid thus obtained is thus precisely the same as in the nematic stasis subject to a field.

This result is somewhat remarkable, when it is recollected that in the orientated solid, cooled to the usual temperature, thermal agitation is considerably less than in the nematic stasis. The small crystals forming the solid orientate themselves, in so far as the nematic stasis itself is orientated.

The following table gives the results of measurements upon paraazoxianisolphenetol:

Temperature.	Physical State.	-χ.10 <sup>7</sup> .
160° C.	Isotropic liquid.	5.62
22° C.	Isotropic solid—in bulk.	5.65
87° C.	Orientated nematic stasis.	4.554
73° C.	Solid orientated by field.	4.550
20° C.	Solid orientated by field.	4.23

It is probable that the small distinct crystals which form the solid obtained when the field is present possess a common direction, and are turned at random about it. For every axis, the least diamagnetism should be very nearly parallel to the field.

The solid orientated by the field is, as a whole, strongly anisotropic:

- (a) Substance in position of crystallisation . .  $\chi=-$  4.53  $\times$  10-7 (b) Substance rotated 90° about axis of cylinder .  $\chi=-$  6.00  $\times$  10-7
- B. Smectic.—The action of a field during crystallisation is far less distinct. If it exists, it is in the opposite sense to that which one would expect: the diamagnetism is greater in absolute value in the direction of the orientating field than in the horizontal direction perpendicular to it. The coefficients of magnetisation observed in the case of ethyl azoxybenzoate are:

Careful observation adds the following information:

The smectic substance is first allowed to crystallise in the field; the latter is orientated with respect to the container along a direction yy'. In the resulting solid the diamagnetism is a minimum along a direction xx' perpendicular to yy' in the horizontal plane. If now the cylindrical container is rotated by 90° about its axis, the direction xx' is parallel to the field, which corresponds, if the magnetic field alone was functioning, to a position of stable equilibrium. The specimen is heated in the field, by progressive melting, beginning at the bottom, and continued until one solid particle remains floating upon the smectic stasis. When this fragment is liberated by melting from all contact with the glass, it is seen to rotate quickly through 90°, and stop in this new position. Perhaps this is a new manifestation of the mutual action between stases.

Observations upon the crystallisation of smectic bodies in a field are still very incomplete in that only a single substance has been investigated, but they are worthy of being followed further. As it is, they bring out another difference, and a very noteworthy one, between nematic and smectic materials.

#### 4. Diamagnetism and Molecular Structure.

Diamagnetism is ascribed to a modification in electronic motion produced by a magnetic field, which modification generates a moment parallel to the field, and in the opposite direction.

In Langevin's theory, the results of which have been confirmed by wave mechanics, an isotropic substance composed of identical atoms having their orientations distributed equally in all directions has a coefficient of magnetisation given by  $\chi = -\frac{N}{4}\frac{e}{m}e^{\tilde{r}^2}$ , where e and m are the charge and mass of an electron, N the number of electrons per unit mass,  $\tilde{r}^2$  the square of the radius of gyration of the electrons of an atom with respect to an axis passing through the centre of gravity. Larmor's theorem deals with the case where the atoms, and consequently the electronic orbits, are orientated. According to this theorem, a circular orbit, radius r, in a plane perpendicular to the field, contributes to  $\chi$  the amount

$$\Delta \chi = -\frac{e^2}{4m}r^2.$$

An orbit in a plane parallel to the field rotates about the field and only furnishes a quantity equal to one-half of the above-mentioned value to the diamagnetism.

This theorem is applicable to the case in which the electrons move under the influence of central forces.

In molecular complexes like those composing mesomorphic substances it is probable that this condition does not obtain. The orbits are, probably, fixed circuits, from which it follows that those situated in planes parallel to the direction of the field make no contribution at all to the paramagnetism.

In the nematic stasis subjected to a magnetic field, the axes of the molecules are along the lines of force; this arrangement has a diamagnetism less than that of the isotropic stasis. This result is at once explicable on the supposition that, in the molecule, there are a preponderating number of orbits contained in the plane parallel to the axis. If the

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temperature rises, thermal agitation causes the orientation to disappear more and more, resulting in a progressive increase in the coefficient of magnetisation. The observed increase in  $\chi$  with temperature, in crass contradiction to the usual constancy of diamagnetism, is then immediately understandable.

If the molecules, unaffected by thermal agitation, could all be rendered parallel, it would be sufficient to measure the coefficient of magnetisation in directions parallel and perpendicular to the axis, in order to obtain data concerning the statistical orientation of the electronic orbits in the molecule. Complete parallelism cannot be achieved in the nematic stasis, but comparison of the properties of nematic para-azoxianisol with those of the crystal shows that in the latter complete orientation is realised in that the axis of the molecules is directed along principle direction 3 (p. 960).

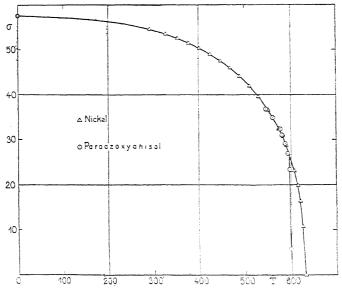


Fig. 8.—Orientation as a function of temperature in the crystal and in the nematic stasis.

Confirmation of this is afforded by the perfect continuity in the values of  $\chi_{is} - \chi_{or}$  which is found on passing from the orientated nematic stasis to the crystal.

Fig. 8 gives the elements of this verification. The curve represents the variation of spontaneous magnetisation with temperature for nickel <sup>18</sup> as a basis of comparison.

On this curve the points denoted by circles show the values of  $\chi_{is} - \chi_{or}$  for para-azoxyanisol. The scale for the ordinates for this substance has been arrived at by making the value of  $\chi_{is} - \chi_{or}$  observed at low temperatures for the crystal coincide with the point representing the spontaneous magnetisation of nickel at the absolute zero. The

 $<sup>^{18}</sup>$  P. Weiss and R. Forrer, Ann. Physik, x, 5, 153, 1926.  $^{19}$  The coefficient  $\chi_3$  of the crystal is extremely insensitive to temperature; extrapolation to the absolute zero can be used without great uncertainty.

scale for the abscissæ has been determined by inserting in the curve for nickel one of the observed values on the orientated nematic stasis.

The remainder of the experimental points fall on the curve. This result would be difficult to explain, if, in the crystal, the axes of the molecules were not all parallel to the direction 3; for example, if they were distributed along two or several directions making definite angles with each other.

Measurements on the crystal of the diamagnetism thus yield the coefficients of magnetisation along the axis of the molecules ( $\chi_3 = -4.08 \times 10^{-7}$ ) and along two directions at right angles to this axis, and perpendicular to each other. According to the theory of diamagnetism quoted already, each of these three coefficients is proportional to the sum of the projections of the areas of the electronic orbits on a plane perpendicular to the appropriate direction. Thus, the sum of the areas of the orbits projected on a plane perpendicular to the axis of the molecule, and on two orthogonal planes passing through this axis are in the ratio of the numbers

There is a marked preponderance of orbits lying in the planes parallel to the chain of carbon atoms. This result, though perhaps not in very good agreement with present ideas on electronic bindings between atoms, deserves extension to other substances.

The preceding example shows that the study of magnetism in the crystal and in the nematic stasis simultaneously, enables one to determine the orientation of the molecules in the crystal, and gives further information concerning the distribution of electronic orbits among three orthogonal planes in the molecule.

It may be hoped that investigations of this nature may be followed simultaneously by theory and experiment.

# INCLINATIONS OF MOLECULES IN SOME CRYSTALLINE-FLUID SUBSTANCES.

By Karl Herrmann (Berlin-Charlottenburg).

Received in German on 2nd January, 1933, and translated by F. I. G. Rawlins.

Nearly all workers have divided crystalline-fluid phases into two classes, following the conceptions and nomenclature adopted by G. Friedel. The first, or "nematic" arises from a parallel arrangement, whereas the second or smectic—always corresponding to lower temperatures—exhibits in addition to this parallel habit another characteristic direction in that both the "heads" and "ends" of neighbouring molecules are arranged in planes.

Friedel supposes that these smectic planes would appear by X-ray analysis, and in fact, de Broglie and E. Friedel have succeeded in obtaining reflection from them. The distance between the planes, calculated by means of Bragg's formula, agrees in order of magnitude with the lengths which are necessitated by the molecules of the substances in question.

The question arises whether it is essential for G. Friedel's idea that the molecules should be placed perpendicularly to these smectic planes. It is stated by de Broglie and E. Friedel 1 that "the chemical formula of smectic bodies, always involving a long rectilinear chain, always leads to considering these chains as orientated parallel to the optic axis, thus along the normal to privileged planes: the distance between homologous points of two successive layers, i.e., the period, must then be at least equal to the length of these chains, and considerable compared with the inter-atomic distances."

The illustrations given by Zocher,<sup>2</sup> Wo. Ostwald,<sup>3</sup> and E. Ott <sup>4</sup> point to the same conclusion.

In addition, the present author and his collaborators have for a long time held the view that a perpendicular arrangement of the molecules is alwavs found.5

In the course of further X-ray work on crystalline-fluid substances, which from their habit may be called smectic, the writer has nevertheless come across two substances, which show wholly similar interferences, to those of de Broglie and Friedel, but which do not yield the same value, calculated from Bragg's equation, for the distance between the planes, as that deduced for the length of the molecule from the atomic diameters. These are the thallium salts of stearic and oleic acids.

First of all, the experimental facts will be reviewed.

The former compound, CH<sub>3</sub>. (CH<sub>2</sub>)<sub>16</sub>. COOTI, has a crystallinefluid phase between the temperatures 118° and 163°, and forms Grandjean's "Gouttes à gradins." X-ray photographs, using filtered Cu-radiation, were obtained by mounting the substance on a small thin glass plate, capable of being rotated backwards and forwards about the horizontal position, 6 so that the different glancing angles could be obtained. The carrier described above was arranged inside a brass tube, which could be heated, and the X-ray entered through a shutter, furnishing a sufficiently great exit-opening; both openings were covered with cellophane windows. The temperature itself, as well as its constancy, was controlled by means of an iron-constantan thermo-element the e.m.f. of which was appropriately registered. The distance between the specimen and the plate amounted to 88 mm. A photograph in the temperature-range corresponding to the crystalline-fluid phase is shown in Fig. 1. The numerical results are given in Table I.

In calculating the length of the molecules, it should be observed that, X-ray work on the fatty acids has given a zig-zag arrangement to the carbon atoms, in which the "bonds" of a C atom form a tetrahedral

angle of 109° 30' with its neighbours.

This entails a distance of 2.54 Å between a pair of C atoms. Further, we take the diameter of the H atoms at the end equal to I Å, and for the oxygens 1.3 Å. An oxygen atom can be assumed to be on one side.

<sup>6</sup> Piece of a cover-glass. Photographs on a mica slip did not yield a different

image.

7 See also on this point, K. H. Meyer and H. Mark, Der Aufbau der hochpolyNew York Tologie 1999, Abschnitt III. See also p. 9, Fig. 3a, meren organischen Naturstoffe, Leipzig 1930, Abschnitt III. See also p. 9, Fig. 3a, where a lauric acid molecule is depicted.

<sup>&</sup>lt;sup>1</sup> M. de Broglie and E. Friedel, C.R., 176, 738, 1923.

<sup>&</sup>lt;sup>2</sup> E. Zocher, Physik. Z., 28, 791, 1927. (Fig. 1b).

<sup>3</sup> Wo. Ostwald, Z. Kristallogr., 79 (Sonderheft), 236, 1931. (Fig. 5c).

<sup>4</sup> E. Ott, Strukturbestimmung mit Rontgeninterferenzen (Handbuch der Experimentalphysik, p. 305, Fig. 177b).

<sup>5</sup> E.g., K. Herrmann and A. H. Krummacher, Z. Kristallog., 81, 317, 1932.

Order.	Distance from Centre in M.M.	an  heta.	$\sin \frac{\theta}{2}$ .	d.
11	3·9	0·0443	0.0222	34·61
2	7·4	0·0842	0.0413	37·21
3	11·2	0·1275	0·0634	36·37
4	15·2	0·1730	0·0855	35·95

TABLE I.—Thallium Stearate—Crystalline-Fluid.  $T = 140^{\circ}$ .

Mean: 36.03 Å

The value 1.5 Å for the univalent thallium ion is arbitrary, since no information can be found in the literature, but a deviation of 50 per cent. from this figure makes practically no difference in the total length.

We then find

$$I(H) + 9 \times 2.54(C - C) + I.3(O) + I.5(Tl^{+}) = 26.7 \text{ Å}.$$

(See Fig. 2).

This value of approximately 26½ Å is quite incompatible with a perpendicular arrangement, and the observed distance between the planes

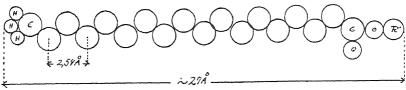
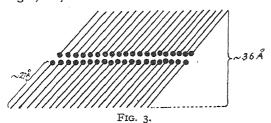


FIG. 2.

of about 36 Å. It makes little difference if we abandon the zig-zag scheme, and assume a linear form with the atoms in series one behind another. This latter model yields a length of 32 Å. Any alternative hypothesis must give shorter distances.

Also, a perpendicular arrangement is not possible with twice the length, i.e., with association into double molecules. Whenever, in the



case of real crystals, with a three-dimensional array of the lattice-particles, the same difficulty arises, we are constrained to assume an inclined arrangement for the molecules.8

In the present

case, also, no other way seems possible than to suppose the existence of inclined double molecules, as depicted in Fig. 3. For the immediate purpose in hand, it is not necessary to decide whether the molecules join up with the end of the acid groups or with the others. The angle, then, which is formed by the sloping double-molecules with the perpendicular on to the planes is found to be 47°.

Any doubts which may be brought against this result may be dis-

<sup>8</sup> A. Müller, Proc. Roy. Soc., 114, 542, 1927, and 120, 437, 1928.

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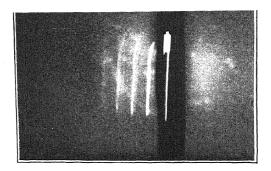


Fig. 1. [See page 973.

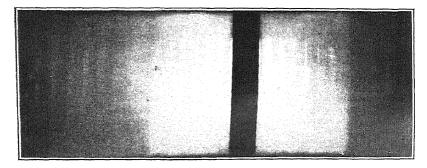


Fig. 4.

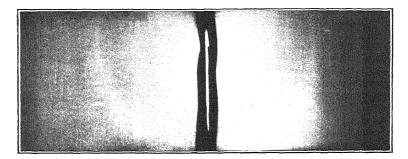


Fig. 5.

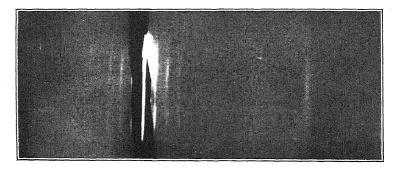


Fig. 6.

persed. Firstly, the objection that the distance between the specimen and the plate is perhaps not accurately measured. It is readily calculated that if the "thickness" of the smectic layers is to be  $26\frac{1}{2}$  Å, then the separation, on the basis of the interference-distances established by the photographs, must amount to 66 mm., and if we take twice  $26\frac{1}{2}$  Å, to 130 mm. This involves an experimental error of 22 mm., or in the second case of 42 mm., which may at once be rejected.

Further, the ratio 1:2:3.... for the observed sine of the semi-angle of deviation shows that, in point of fact, the orders of the interferences are correct.

Finally, it might be assumed that the solid phase was present, and not the crystalline-fluid. This presumption can be rejected by using the same apparatus for taking photographs at room temperature. Fig. 4 shows a photograph of the solid phase, while the calculations are contained in Table II.

Order.	Distance from Centre in mm.	$\tan \theta$ .	$\sin \frac{\theta}{2}$ .	d.
1 2 3 4 5 6 7	6·5 9·6 13·1 16·2 19·6 23·0	0.0739 0.1096 0.1482 0.1846 0.2221 0.2613	0.0369 0.0546 0.0736 0.0911 0.1091 0.1275	41.65 42.22 41.77 42.18 42.26 42.19

TABLE II.—THALLIUM STEARATE CRYSTALLINE-SOLID.

Mean: 42.05 Å.

The inclination here amounts to about 37°. Table III gives the measurements and calculations for Thallium Oleate in the crystalline-

Order.	Distance from Centre in mm.	tan θ.	$\sin \frac{\theta}{2}$ .	đ.
ı	4.3	0.0466	0.0234	32.84
2	4·2 8·5	0.0966	0.0482	32·84 31·89
3	12.3	0.1399	0.0695	33.16
4	17.5	0.1988	0.0980	31.37

TABLE III.—THALLIUM OLEATE. CRYSTALLINE-FLUID.

Mean: 32.3 Å.

fluid state; and Table IV for the same compound in the crystalline-solid state. Figs. 5 and 6 are the corresponding photographs.

The calculation of the length of the molecule proceeds in a similar way to that for the stearate, with the help of the formula:

$$\begin{array}{l} H_3C - (CH_2)_7 - CH = CH - (CH_2)_7 - COOTI & I(H) + I \cdot 54 (C) + 3\frac{1}{2} \\ \times 2 \cdot 54 (C - C) + 2 \times I \cdot 54 (C = C) + 3\frac{1}{2} \times 2 \cdot 54 (C - C) + I \cdot 54 (C) + \\ I \cdot 3 (O) + I \cdot 5 (TI') = 27 \cdot 7 \text{ Å}. \end{array}$$

This accounts for the unsaturated CC-group in the centre.

We are thus compelled in this case also to assume the presence of double molecules, with an inclination in the crystalline-fluid state of about 53° and in the crystalline-solid state of about 34°.

For both salts, the molecules in the crystalline-fluid phase slope more steeply than in the crystalline-solid phase.<sup>9</sup>

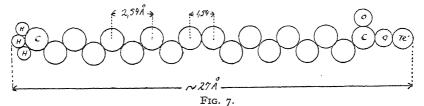
	J 111 11111111111111111111111111111111		OIL CAMBBAILD	
Order.	Distance from Centre in mm.	tan θ.	$\sin \frac{\theta}{2}$ .	d.
1 2 3 4 5	3.0 6.0 9.1 12.1 15.2	0·0342 0·0682 0·1034 0·1376 0·1722	0.0172 0.0341 0.0515 0.0684 0.0852	44.68 45.07 44.77 44.94 45.10

TABLE IV.—THALLIUM OLEATE. CRYSTALLINE-SOLID.

Mean: 44.9 Å.

Interferences other than those from the greatest smectic plane-toplane distances could not be perceived from the X-ray photographs. Nothing can be said about the arrangement, or lack of arrangement, of the molecules in the planes.

It might seem that the conception developed in an earlier investigation <sup>10</sup> into the transition of crystals in liquid phases could be applied here also. The crystal "melts" first along such lattice planes (the pinacoidal) which correspond to the long crystal-axes of which the



lattice distance is thus greater compared to the other two. In these directions the substance continues to hold together (in orderly array or in disorderly) on attaining a still higher temperature.

The inclination of the molecules then changes, and sometimes becomes perpendicular, or sometimes, as in the present instance, more steeply sloping. Further experiment is needed in order to be in a position to say when one or the other will occur.

The size of such complexes reaches colloidal dimensions. In the opinion of the author, it is not essential that a phase composed of such large particles should behave as a powder, and should not exhibit the characteristics of a fluid. There are, on the other hand, organic substances, with giant molecules, which pass over, on heating, into true, although tenacious, fluids.

I wish to thank my collaborators, Mr. A. H. Krummacher and Mr. L. Brenner, whose assistance in this investigation has been very great.

<sup>&</sup>lt;sup>9</sup> For phenylbenzalamino cinnamic acid ethyl ester and terephthalbisamino cinnamic acid ethyl ester (K. Herrmann and A. H. Krummacher, Z. Kristallogr., 81, 317, 1932), which of course belong not to the aliphatic but to the aromatic compounds, the behaviour is the reverse of the above; the molecules become more upright for the transition to the crystalline-fluid state from the crystalline-solid state.

<sup>&</sup>lt;sup>10</sup> K. Herrmann and A. H. Krummacher, *loc. cit.*, on p. 331. This form of conception of the smectic phase is very like the lamellar-dispersed state of matter visualised by Wo. Ostwald.

# ROTATING MOLECULES AND THE LIQUID CRYSTALLINE STATE.

AN X-RAY EXAMINATION OF LONG CHAIN ESTERS.

By T. Malkin.

Received 31st March, 1933.

The normal esters of long chain acids \* have many properties in common with typical liquid crystals; for example, their liquid phase solidifies to a liquid-like transparent mass, which becomes crystalline on further cooling; further, they form with each other, unbroken series of solid solutions without temperature minima, and finally, microscopic examination shows that they exist in a form which is uniaxial and positive, with the optic axis perpendicular to the microscope slides.2

For these reasons, the esters appear to be suitable substances for the examination of certain liquid crystal properties. I shall therefore discuss the investigation of the esters and then consider whether the conclusions drawn may be applied to the problem of the liquid crystalline state.

The esters examined are a number of propyl, butyl and amyl esters of palmitic, margaric and stearic acids, which, like the ethyl esters, 4 are found to exist in two forms.

On cooling the melted ester there first separates a transparent solid, which, on further cooling, becomes white and opaque, and shows a more definite crystalline structure. The two forms are termed respectively the  $\alpha$  and  $\beta$  modifications, in harmony with the terminology of Garner and Randall,5 who observed similar phenomena in the case of the odd fatty acids.

The changes are well shown by cooling curves on which there are two distinct arrests, usually some five or ten degrees Centigrade apart. Margarates exhibit enantiotropic dimorphism, i.e., the change  $\alpha - \beta$  is reversible. This is shown by heating curves, on which there are also two arrests, almost coincident with those on the cooling curves. Palmitates and stearates, however, appear to be monotropic, since there is only one arrest on the heating curve, corresponding to the ordinary melting-point. It appears, therefore, that if the change  $\alpha$ - $\beta$  is reversible in the latter cases, the transition temperature is practically coincident with the melting-point.

The main conclusion drawn from a study of the cooling and heating curves is that margarates assume the  $\alpha$  form much more readily than palmitates and stearates.

\* Excluding the methyl esters.

Mr. C. E. Clarkson.

<sup>4</sup> T. Malkin, Nature, 127, 126, 1931; J.C.S., 2796, 1931; J.C. Smith, loc. cit.; J. W. C. Phillips and S. A. Mumford, J.C.S., 1732, 1931.

<sup>5</sup> W. E. Garner and F. C. Randall, J.C.S., 125, 881, 1924.

<sup>&</sup>lt;sup>1</sup> J. C. Smith, J.C.S., 802, 1931; S. A. Mumford and J. W. C. Phillips, Rec. Trav. Chim., 52, 182, 1933; D. Vorländer, Z. Krist., 70, 80, 1931.

<sup>2</sup> D. Vorländer and W. Selke, Z. physik. Chem., 129, 449, 1927.

<sup>3</sup> Full experimental details will shortly be published in a joint paper with

The X-ray examination was carried out as previously described,6 the a forms being examined a few degrees below the melting-points.

The long spacings, in Angstrom units, are given in Table I, together with those of the methyl and ethyl esters.

TABLE I
---------

		Palmitate.		Margarate.		Stearate.
	α.	β.	α.	β.	α.	β.
Methyl Ethyl Propyl Butyl Amyl	27·6 28·8	$\begin{cases} 21.6 \\ 23.0 \\ 23.8 \end{cases} \text{ diff.} = 1.4 \\ 23.8 \end{cases}$	27·1 28·6 30·1 31·45	$ \begin{array}{c} 23.3 \\ 24.6 \\ 3 \end{array} $ diff. = 1.3 $ \begin{array}{c} 25.5 \end{array}$	28·6 30·1 31·4	23.9 diff. = 1.6 25.5 diff. = 0.7 26.2 diff. = 1.5 27.7 diff. = 1.1

The spacings of the  $\alpha$  forms correspond to planes separated by vertical zig-zag chains, whereas those of the  $\beta$  forms, which are shorter, correspond to tilted chains. The main point of interest connected with the X-ray examination is, however, that the a forms give only one side spacing of 4.2 Å, whilst the  $\beta$  forms give the two side spacings usually associated with long chain compounds, viz., 3.7 and 4.2 Å.

The esters thus appear to behave in a similar manner to the paraffins 7 and the alcohols.8 where the absence of the shorter side spacing in the α form is attributed to rotation of the molecule about the chain axis.

The probability of molecular rotation in crystals has recently been theoretically examined by L. Pauling 9 and T. E. Stern, 10 who have been able to indicate the necessary conditions. In the simplest terms, rotation may be expected when I, the moment of inertia about the rotation axis, and V, a potential function representing the interaction of the molecule with surrounding molecules, are both small. In the case of long chain compounds these conditions are frequently satisfied, and on raising the temperature of the solid, rotation about the chain axis may set in before melting.

This theory appears to solve a number of crystallographic problems; 11 in particular, it removes Hendricks' objection to the zig-zag carbon chain <sup>12</sup> and satisfactorily explains the disappearance of the shorter side spacing of 3.7 Å which usually occurs a few degrees below the meltingpoint. It is not difficult to see that a system, which could be regarded as being composed of long narrow rotating rods, could form a symmetrical hexagonal arrangement more readily than a system of rigid zig-zag chains.13

T. Malkin, J.C.S., 2796, 1931.
 A. Müller, Proc. Roy. Soc., 127A, 417, 1930; 138A, 514, 1932.
 J. D. Bernal, Z. Krist., 83, 153, 1932.
 L. Pauling, Physical Rev., (ii), 36, 430, 1930.
 T. E. Stern, Proc. Roy. Soc., 130A, 551, 1931.
 See J. C. Southard, R. T. Milner, S. B. Hendricks, J. Chem. Physics, 1, 95, for fuller references 1933, for fuller references.

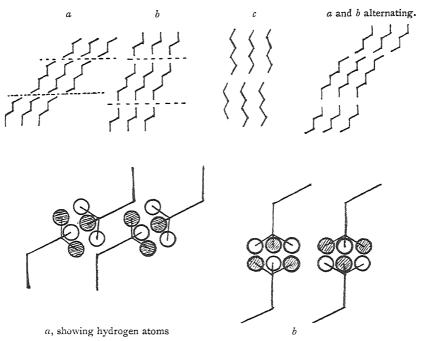
12 S. B. Hendricks, Z. Krist., 68, 189, 1928; 74, 29, 1930.

<sup>13</sup> A. Muller, Nature, 129, 436, 1932; Proc. Roy. Soc., 138A, 514, 1932.

It is now of interest to consider why the margarates assume the  $\alpha$  form more readily than the palmitates and stearates.

I have suggested elsewhere,  $^4$  that physical differences between odd and even members of homologous long chain compounds are due to differences in the packing of the terminal planes, and it seems probable that this might explain the lower stability of  $\beta$  form of the margarates. It is therefore of importance to examine the orientation of these planes; but before doing so, the simpler case of the paraffins may be considered with advantage.

A comparatively rigid zig-zag carbon chain admits of two extreme positions for the terminal methyl groups, namely, a and b (Fig. 1), which



Shaded spheres project forward, unshaded backward. The planes are indicated by discontinuous lines.

Fig. 1.—Types of terminal planes (diagrammatic).

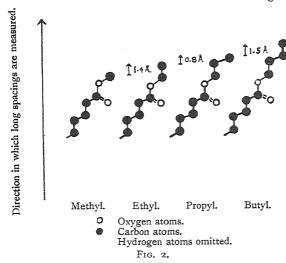
may occur in the case of even tilted chains; c is intermediate and exists in the case of a vertical chain, whilst a and b occur alternately in odd tilted chains.

The main attractive forces operating about these planes are presumably those between hydrogen nuclei and the electrons surrounding the carbon atoms, consequently the potential function V would be expected to be greater, the more readily the hydrogen atoms can form lateral contacts with carbon. It will be clear from Fig. 1 that V is greatest in position a, least in b, and of intermediate value in c. In order, therefore, to reach a state of lowest potential energy, the molecules will tend towards arrangement a rather than b.

The above considerations throw much light on certain unexplained properties of the hydrocarbons. It has long been known, mainly from

the work of Müller, that the odd numbered members always possess a vertical chain, whereas even members may have vertical or tilted chains according to temperature conditions. It is obvious that even chains can readily tilt to form series of terminal planes of the favoured type a. Odd chains, however, cannot do this, since formation of type a planes at one end necessarily involves the formation of type b planes at the other. These two processes are diametrically opposed, and consequently the chain remains vertical. Again, as would be expected, it is known that the even members of the lower paraffins crystallise more readily than the odd, 14 and that the zero point volume of the odd members is greater than that of the even. 15 Lastly, Piper and Chibnall have shown that the change  $\beta$ - $\alpha$  takes place at a relatively lower temperature with the odd than with the even paraffins. In other words, rotation sets in more readily when the potential V is smaller.

The case of the esters and of most other long chain compounds differs



from that of the paraffins in that there is a polar group at one end of the chain. As a rule, such polar groups are compared with the distance between the hydrocarbon chains,17 and sequently, in order to form lateral contacts, they tend to form type a planes. It follows that the size and polarity of these groups determine whether, and to what extent, the chain tilts.

The arrangement of the various groups in the esters can be deduced with a high degree of probability from the X-ray data of the  $\beta$  form. It will be seen that passing from methyl to ethyl esters causes an increase in length of 1.4 Å (mean); from ethyl to propyl, 0.8 Å; from propyl to butyl, 1.5 Å; from butyl to amyl, I·I Å. There is thus a well marked alternation which indicates that the terminal planes of the ester groups in ethyl and butyl esters are of the loosely packed b type. Fig. 2 illustrates this point.

If, in addition, account is taken of the slightly greater relative lengths of the margarate molecules, it is possible to make the following deductions. (I) The carboxyl group has the same orientation with respect to the chain in all the esters; (2) the ether oxygen valencies are inclined at an angle which approximates to the tetrahedral; (3) the terminal methyl planes

D. Vorländer, Z. Krist., 79, 70, 1931.
 W. Biltz, W. Fischer, E. Wunnenberg, Z. physik. Chem., 151A, 38, 1930.

S. H. Piper, A. C. Chibnall, and others, Biochem. J., 25, 2082, 1931.
 W. E. Garner, F. C. Madden, J. E. Rushbrooke, J.C.S., 2497, 1926.

of the acid chain are of the type a in the palmitates and stearates, but of type b in the margarates.

Although it is thus possible to deduce the type of both terminal methyl planes of the esters, the latter cannot be treated in the same simple manner as the paraffins, since it is clear from a consideration of their melting-points that some other factor is operating.

It has been shown by Adam 18 for the palmitates, that as the ester chain increases in length the melting-points fall. This effect appears to be quite general, and is illustrated by the following setting points of the stearates:-

It is difficult to account for this unusual behaviour unless one assumes that it is due to the flexibility of the ether oxygen link, and consequent facile rotation of the ester chain. This view, which seems incidentally to offer an explanation of the ready expansion of ester films, 18 would be in harmony with current ideas on the anomalous dipole moments of certain ether oxygen compounds, e.g., the quinol ethers. The latter subject has been investigated by Meyer, 20 who has shown that in most cases the energy of thermal agitation kT will exceed the intramolecular potential of the dipoles at ordinary temperatures and that consequently the ether group will rotate. More specifically, he states that the potential varies inversely as the cube of the distance between the dipoles (d), and that for dipoles of the magnitude I  $\times$  10 <sup>- 18</sup> E.S.U., the thermal energy at ordinary temperatures,  $kT(4 \times 10^{-14})$  ergs, will equal the potential if d=3 Ångstrom units. In the esters the moment is of the order  $1.9 \times 10^{-18}$  E.S.U., and d is between 4 and 5 Å, so that rotation is possible at ordinary temperatures.

The picture of the esters is now more complete, and offers an explanation of the enantiotropism of the margarates. In the latter, the zig-zag chain, of low moment of inertia, is attached to two terminal groups, both capable of ready rotation, whereas in palmitates and stearates, the terminal plane of the acid chain is of type a and more rigid. Hence it would be expected, that on raising the temperature, margarates would more readily set into a state of complete rotation  $(\beta-\alpha)$  than palmitates and stearates, whilst on cooling the latter should more readily change to the stable  $\beta$  modification. Both these expectations are in accordance

#### with facts.

#### The Liquid Crystalline State.

The suggestion I wish to make to this meeting for discussion is that in the liquid crystalline state the molecules are rotating about their long axis, which is aligned perpendicular to the planes formed by the terminal groups. In other words, the condition of the  $\alpha$  form of the esters is typical of the liquid crystalline state.

Structurally, liquid crystalline substances are like the esters in being long molecules, with weak attractive forces both laterally and terminally. In most cases the terminal groups contain mobile ether oxygen groups

<sup>&</sup>lt;sup>18</sup> N. K. Adam, Proc. Roy. Soc., 101A, 528, 1922.

<sup>19</sup> The melting-points begin to rise again between Amyl and Octyl. Adam,

<sup>20</sup> L. Meyer, Z. physik. Chem., 8B, 27, 1930. See also L. Ebert, Dipole moment and chemical structure, p. 43. Blackie.

or other groups, which from dipole measurements are regarded as being readily capable of rotation (—NHR.—NR<sub>2</sub>). Moreover, in many cases the lateral forces are weakened by the presence of mutually repelling electron centres such as double and triple bonds.

From the above, it will be clear that all the conditions are favourable for rotation. I, the moment of inertia, and V, the potential, are small, and according to the character of the terminal groups, monotropic or enantiotropic changes may be expected. Further, dependent on the peculiarities of the molecule, other states could be inferred where only sections of the molecule are in complete rotation.

Unfortunately, there are very few data in the literature on the long spacings of liquid crystals, but Friedel <sup>21</sup> has shown that for ethyl para-azoxy benzoate the long spacing increases from  $16\cdot 2$  Å in the crystalline state to 19.9 Å in the smectic, a result which suggests a change from a tilted to a vertical arrangement. In view of this paucity of data, I propose to investigate a series of compounds of the type X-X(Y), where the terminal groups are joined by phenylene and diphenylene groups. By suitable substitutions it should be possible to control both I and V.

Finally, I should point out that the idea of uniaxial rotation is not new, since it has been suggested by Vorländer and Selke,<sup>2</sup> and is also given in Beckenkamp.<sup>22</sup> My own contribution is its experimental realisation by means of X-rays and the recognition of the part played by the terminal groups.

I have pleasure in acknowledging generous grants from the Royal Society and the Colston Society.

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E. Friedel, Compt. rend., 180, 269, 1925.
 Borntraeger, Leitfaden der Kristallographie, p. 443, 1919.

# ALTERATIONS IN THE NATURE OF A FLUID FROM A GASEOUS TO LIQUID CRYSTALLINE CONDITIONS AS SHOWN BY X-RAYS.

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Received 3rd January, 1933.

From X-ray diffraction observations it appears that ordinary liquids, more especially those having asymmetrical molecules, consist chiefly of aggregates or groups, but also in part of molecules having a much more random distribution. In these groups (called "cybotactic") there is evidenced, through coherent X-ray interference, a distinct semi-orderly molecular array, but some of the more random molecules scatter X-rays practically as would the same molecules in a gas. The experiments of Hückel 1 and the author 2 show that the coherent X-ray diffraction in

<sup>&</sup>lt;sup>1</sup> E. Hückel, *Physik. Z.*, **22**, 56, 1922. <sup>2</sup> G. W. Stewart, *Physic. Rev.*, **38**, 931, 1931.

the liquid crystal and the transparent liquid of para-azoxyanisol are practically the same, but from additional evidence of the latter author the conclusion will here be reached that the liquid crystal is a large aggregate of similarly oriented cybotactic groups; it is a huge regiment of small companies of molecules. Thus the small cybotactic groups in the liquid which are brought into evidence through X-ray measurements become optically anisotropic when approximately aligned with each other over a region dimensionally comparable to an optical wave-length. This is the description of a liquid crystal that is obtained through investigations with X-rays. Its modification and expansion will depend upon the extension of present experiments.

Obviously the acceptance of the conception just stated depends upon the confidence which should be placed in the interpretation of the X-ray observations with ordinary liquids as well as those with liquid crystals. Are there really at any instant in a liquid molecular aggregates which crudely simulate fragments of crystals? Would not the space occupied by the molecules prevent completely random distribution? Is this not really a step in the direction of orderliness, and therefore will this not be a sufficient interpretation? May not the results be explained without assuming the influence of molecular forces? It is because of such reasonable doubts that the discussion of observations on liquid crystals may advisedly be prefaced by explanations of observations on liquids and gases. This is the plan followed in the accompanying paper, but brevity requires that the justification for some of the statements must be left to previously published discussions.

#### The Use of X-rays.

In the liquid there are two opposing tendencies. The cohesional forces seek to produce condensation and solidification, but the application of heat has the opposite effect, melting solids, and separating liquid molecules into vapour. Cohesion is an evidence of potential energy and temperature of kinetic energy. In a liquid there is a constant shifting of a molecule from one form of energy to another, the statistical result being a condition of minimum energy. A knowledge of this internal condition must, in the absence of information concerning the molecular forces, be obtained through experiment.

In the use of X-rays as a tool of investigation one can place full confidence in the assumptions that, (I) the classical theory of scattering is sufficiently approximate in the region of small angular diffraction used in our experiments; (2) the incoherent diffuse scattering in this small angular region may be omitted from consideration; (3) the bands formed with liquids are caused by interference either between the molecules or within the molecules. Through the work of Debye 3 and his collaborators the production of diffraction bands by the arrangement of atoms in the molecules has been studied, and there is excellent agreement between the anticipated and the realised results. The diffraction bands in liquids to which reference will here be made occur at smaller angles, and are clearly caused by the distance of separation of molecules. The curve of the classical scattering of X-rays by an electron is shown in curve I of Fig. I. If the atom of the gas contains several electrons, the scattering from each electron in the atom will not be in phase with that from the others except

 $<sup>^3</sup>$  Article by Menke, *Physik. Z.*, 16, 593, 1932, contains references to the literature.

at the angle of scattering, o°. Everywhere else there will be interference, and consequently the scattering curve will have a more rapid

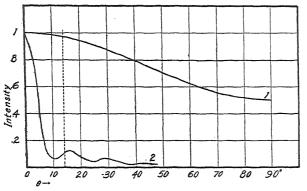
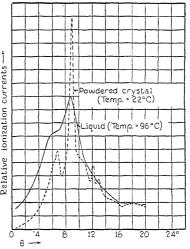


Fig. 1.—Curve r is the classical scattering of X-rays by an vertical dotted electron. Curve 2 is the theoretical classical scattering line represents per electron in CCl<sub>4</sub>.

descent. Then, in addition there are several atoms in each molecule. sharply dropping curve will contain bands shown in curve 2 of Fig. 1. This is a theoretical curve of Debye for CCl<sub>4</sub>. The wave-length used is MoKα. The line represents the small angle

within which the observations of this paper are concerned. The nature of the diffraction curve with a liquid in this region is shown in Fig. 2. With the same apparatus (ionisation chamber, electrometer, approximately monochromatic  $MoK\alpha$  radiation) and the same mass of triphenylmethane, transmission diffraction curves were taken for both the liquid and solid. The typical liquid curve consists of bands and these appear, as has been shown by the numerous experiments of Krishnamurti  $^4$  and

others, to occur at approximately the angular regions in which the intensity-density of the diffraction lines of the powdered crystal is large. If one can be confident that the diffraction bands with liquid are not caused merely by the volume-effect of molecules, but by a coherence of the radiation from the molecules existing at the moment in imperfect, semiorderly molecular groups, the presence of the X-ray diffraction bands can be interpreted as showing the presence of such groupings in the liquid. This confidence is enhanced by the fact that there are molecules of different compounds which have approximately the same shape yet which do give markedly bands. Moreover, there are now in evidence the results from a variety of liquid experiments, all



different diffraction Fig. 2.—X-ray diffraction of the same eover, there are now mass of liquid and powdered crystal triphenylmethane.

of which are in conformity with the conclusion that the diffraction bands,

<sup>&</sup>lt;sup>4</sup> Krishnamurti, Ind. Jour. Physics, III, 11, 225, 1928, and also Stewart and Morrow, Physic. Rev., 30, 232, 1927; and Morrow, Physic. Rev., 31, 10, 1928.

such as dealt with in this article, must be caused by crude but definite semi-orderly grouping of molecules. The literature must, of course, be examined to acquire a confidence in this view. It seems fair to claim that the experiments in the author's laboratory and elsewhere have now reached a stage where a crude description of the interior of a liquid can be given with considerable confidence. At any instant the molecules are found roughly in one of two classes. Either they are in cybotactic groups, in semi-orderly array, strongly imitating fragments of crystals, or they have comparative freedom. That such a liquid would produce a diffraction band as in Fig. 2 is evident when one considers that the groups are small, perhaps of the order of 100 to 1000 molecules each, that they are not sharply defined, that they are not perfectly regular, that there is a fluctuating density in the liquid, and that the shape of the molecules cannot be considered as constant. Moreover, the liquid curve does not approach a zero value as the angle of diffraction approaches oo, but nearly so. This additional difference between the effects of a crystal

fragment and of the liquid may be regarded as caused by the presence in the liquid of a few molecules sufficiently at random to give a rapidly falling scattering intensity near 0°, as in curve 2, Fig. I. In the necessary absence here of all of the evidence for substantiating the cybotactic view, one may make the additional remark that the more the interior structure of the liquid is studied the greater is the apparent similarity with crystals. This is, of course, because the same molecular forces are in action in both cases. Of course, an individual cybotactic group does not remain There is the constant intact. shifting of molecules in and out of recognizable groups and constant slippage of the approximate planes in these cybotactic groups. The point is that the molecules are grouped in a very imperfect and temporary yet importantly significant manner. The classification of the molecules at any instant into those that are in cybotactic groups and those that are comparatively free is arbitrary. In fact, there are all the

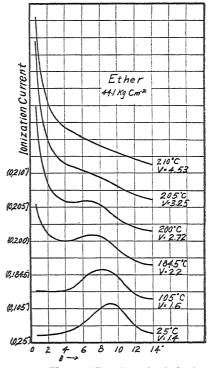


Fig. 3.—X-ray diffraction of ethyl ether near the critical point, 36·7 kg/cm.², 194·6° C., and 3·77 cm.³/g.

possible gradations between. It is to be hoped that the subsequent discussion, with experimental results, will give additional confidence in the foregoing view upon which is based the interpretation of the X-ray results.

<sup>&</sup>lt;sup>5</sup> A brief review of the evidence for the cybotactic view of the interference of liquids is just being published in the *Indian Journal of Physics*.

# Internal Changes in Passage from a Gas to a Liquid.

Recently Waldemar Noll <sup>6</sup> and R. D. Spangler <sup>7</sup> have investigated the change in the X-ray diffraction of ethyl ether in the *p-v-t* region near the kg./cm.<sup>2</sup>, critical point, Fig. 3. The critical values for ethyl ether are <sup>8</sup> 36·7 194·6° C., and 3·77 cm.<sup>3</sup>/g. The conditions in these observations in Fig. 3

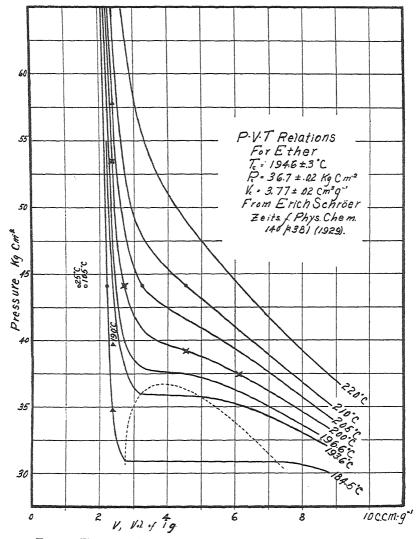


Fig. 4.—The p-v-t relations of ethyl ether, according to Erich Schröer.

are indicated in Fig. 4 by the small circles. In Fig. 3 the curve for 210° C. has the shape of a typical gas diffraction curve. The one for 25° C. is a typical liquid curve. All the curves are combinations of the two types.

Noll, Physic. Rev., 42, 336, 1932.
 Schröer, Z. physik. Chem., 140, 381, 1929.

It is noticed at once that as the temperature is increased, there is less evi-

dence of cybotactic groups and more of random gas-like molecules. The material is not homogeneous, and any attempt, such as in van der Waals' theory to use homogeneity as a basic assumption, must result in an inadequate description of what transpires. In none of the cases in Fig. 3 is the ethyl ether in the liquidvapour two-phase region, yet there is clear evidence of the cybotactic groups. According to the usual definition, "liquid" refers to one of the components in the two-phase region The term is made mentioned. to depend, not upon the internal disposition of molecules, but upon the possibility of a second phase (vapour) in equilibrium. Yet here, as shown in Fig. 3, we have cybotactic groups formed without the substance being regarded as a liquid. It is also observed from Fig. 3 that the cybotactic groups are not de-

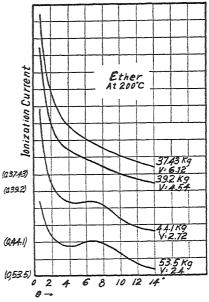


Fig. 5.—X-ray diffraction in ethyl ether at 200° C. and several values of pressure and specific volume.

pendent upon the critical temperature, 194.6° C., but exist at temperatures both higher and lower than that value.

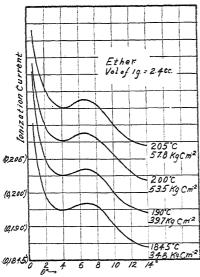


Fig. 6.—X-ray diffraction in ethyl ether at constant specific volume.

In Fig. 5 are shown the observations at a constant temperature, 200° C., which is somewhat above the critical one. The values of p, v and t for these observations are indicated in Fig. 4 by the crosses. Fig. 5 shows that the cybotactic groups exist at specific volumes below the critical one, but not at specific volumes greater than this value.

In Fig. 6 are shown observations with a constant specific volume 2.4 cc./g., which is less than the critical one, 3.77. conditions of these observations the small indicated by In Fig. 6, triangles in Fig. 4. as in Figs. 3 and 5 also, corrections have been made to reduce the observations to equal masses. Consequently, it is seen in Fig. 6 that the cybotactic grouping remains the same over the variation of pressure and temperature used. The evidence from these constant volume experiments is thus that the existence of the cybotactic groups depends upon the specific volume more importantly than upon pressure or temperature.

The experiments near the critical point are yet in progress, but the conclusions that can now be drawn for ethyl ether doubtless have a rather general significance. We must needs revise our conception of liquefaction. It is not the process of formation of aggregates by coalescence. It is not determined by the fractional number of molecules that are in cybotactic groups. We are to recognise that when molecules are held by pressure in sufficiently close proximity they will form small temporary cybotactic groups wherein the molecules are arranged in an orderly manner crudely imitative of fragmentary crystals. On account of our lack of knowledge of the interior we have come to refer to a condition as the "liquid state" which does not depend upon the extent of this internal grouping, but upon the possibility of another phase, less dense, which is in equilibrium therewith.

These experiments show the persistence of the cybotactic groups. They are always present in a liquid, and at ordinary temperature the percentage of molecules not in such groups at any instant is small. For example, in the case of ethyl ether at room temperature it appears that perhaps 7 to 10 per cent. of the molecules scatter X-rays as would a gas. One can see that with ethyl ether the change in the internal character, as a substance is caused to pass from the gaseous to the liquid state, is a continuous one. Doubtless the case of ethyl ether can be accepted as typical.

## Internal Change in Passing from a Liquid to a Liquid Crystalline Condition.

In the experiments to which reference will now be made, the substance para-azoxyanisol was examined by X-ray diffraction. It may be taken as a representative of the cases where the crystal melts into a turbid anisotropic liquid which at a higher temperature becomes transparent and optically isotropic. Both transitions with para-azoxyanisol are sharp. As early as 1921, Hückel 1 examined para-azoxyanisol and found that the transmitted diffraction pattern with the liquid crystal and the transparent liquid were identical. But the more quantitative results of the author 9 show an interesting difference in the diffraction intensity. A brief account of not only this evidence but also other accompanying results will add to the clearness of subsequent discussion.

The purpose of the experiments mentioned was a study of the magnetic character of para-azoxyanisol. It had been known for a number of years that the magnetic field would orient para-azoxyanisol liquid crystals, optical 10 and X-ray 11 tests agreeing in this conclusion. In the author's experiments the MoKa rays 12 were transmitted through a sample of para-azoxyanisol perpendicularly to the direction of the magnetic field. Fig. 7 shows the diffraction intensity curve with the field zero and 1300

<sup>&</sup>lt;sup>9</sup> Stewart, *Physic. Rev.*, **38**, 931, 1931.

<sup>&</sup>lt;sup>10</sup> Mauguin, C.R., 152, 1680, 1911.

<sup>11</sup> Kast, Ann. Physik, 73, 145, 1924.
12 The voltage on the tube was left low enough to avoid any noticeable effects of general radiation and a zirconium filter produced an approximately homogeneous radiation.

gauss at a temperature of 128° C.13 One peak disappears with the action of the field, and another appears. The disappearance indicates a prac-

tically complete orientation of the large groups, so that the chief diffraction planes become parallel to the plane containing the spectrometer angle,  $\theta$ . The small peak is doubtless caused by diffraction from a different set of planes, the effect of which the magnetic field has brought more into prominence. The other results pertinent to the current discussion are as follows:—

I. If the containing tube be rotated, the effect of the magnetic field is very materially altered. When the tube, approximately I cm. in diameter, is rotated once per second, the effect of the field is reduced to two-thirds.

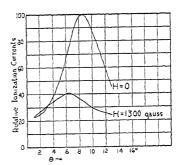


Fig. 7.—X-ray diffraction in liquid crystalline para-azoxyanisol at 128° C., with and without the magnetic field of 1300 gauss.

If the rotation is twice per second, only about one-fifth of the effect remains. These results were obtained with a field 2100 gauss, which produced approximately complete orientation of molecules.

2. The diffraction-intensity curve for the transparent liquid at 143° C. is practically that shown for the milky liquid at 128° C. in Fig. 7. But the diffraction intensity of the latter is approximately 10 per cent. greater throughout the range tested. This indicates greater X-ray coherence in the liquid crystalline condition.

3. The effect of a magnetic field of 2210 gauss upon the chief intensity maximum diffraction, with the transparent liquid at 143° C., and with zero speed of rotation of the sample, was found to be 0.2 per cent., an amount less than the error in the experiments.

4. The milky liquid was frozen while in a field of more than 6000 gauss. While in the milky liquid the molecular groups are fully oriented with this magnetic field, yet when frozen there no longer exists any evidence of the effect of the field. This is shown by the fact that the major diffraction peak of the crystal at 9.25° is the same intensity whether the substance is frozen with or without the presence of the field. On account of chance preferential directions in freezing, this result was derived from the average of ten trials of sudden freezing in the magnetic field.

5. The effect of an alternating field was quite marked. For a given effective current in the electromagnet, making H=1100, the alternations were varied from 18 to 105 cycles. With the former the effect of the magnetic field was 60 per cent. that obtained with continuous current. With the latter it was 11 per cent.

The conclusions, both old and new, that seem to be almost inevitably drawn from the above are:—

I. The grouping of molecules in the liquid crystal is different than in the liquid, the groups being very much larger in the former. This is shown by the easy influence of the magnetic field and the effect of mechanical disturbance. Upon the cybotactic groups in the transparent liquid neither of these physical conditions produce any effect. This

 $<sup>^{13}\, \</sup>text{The solid}$  melts at 117° C. and the liquid becomes transparent and optically isotropic at 134° C.

difference in grouping, of course, agrees with the difference in optical

anisotropy.

2. The semi-orderly molecular arrangement in both the liquid crystal and the liquid is almost the same, as judged by X-rays, but with the groups in the former producing a slightly greater coherence in the diffraction.

3. X-ray and optical tests both agree in that the relatively large groups in the liquid crystal do not exist in the liquid. But the X-raye show the persistence of the cybotactic groups in both conditions. The most simple and direct explanation is that the liquid crystal is a regiment of many small companies of molecules or of cybotactic groups. The alignment of one minor group with others in the large major group is not sufficiently perfect to increase very noticeably the intensity of X-ray diffraction or the sharpness of the bands, but it is sufficient to provide a region in the liquid crystal that is distinctly anisotropic for an optical wave-length.

The conclusion just drawn for para-azoxyanisol is that the cybotactic groups in the transparent liquid become aggregated in the liquid crystal, with approximately similar orientation, into relatively enormous groups. If a cybotactic group contains perhaps 100 to 1000 molecules, then the liquid crystal regiment of these companies must have as a minimum the dimension of the order of a wave-length of light, or it must contain perhaps a million times as many molecules. The result for para-azoxyanisol is not presented with the expectation of concluding that the case may be regarded as perfectly general. But it undoubtedly may be considered as having a rather wide application to liquid crystals which have a temperature range between that of the solid and isotropic liquid states. Moreover, the extensive experiments of X-ray diffraction in gases and liquids now give a picture of the significant effects of atomic and molecular forces, most ideally exemplified in the stable configuration known as a crystal.

# NOTE ON THE ARRANGEMENT OF CHAIN MOLE-CULES IN LIQUID *n*-PARAFFINS.

By Alex. Müller (Davy-Faraday Laboratory, Royal Institution).

Received 27th March, 1933.

In the course of an investigation of the structure of solid paraffins near their melting-points, the writer made reference to the arrangement of chain molecules in the liquid. The problem of the liquid state was not discussed in detail as it was outside the scope of the investigation. The present note, which does not introduce essentially new facts, deals in more detail with the difficulties of the interpretation of the diffraction rings obtained with liquid chain compounds.

Examination of solid paraffins near their melting-points has shown that the chain molecules are arranged like closely packed hexagonal

pencils.

A theory has been put forward by G. Stewart, 2 according to which the liquid paraffins are in a semi-crystalline or "cybotactic" state. The

<sup>&</sup>lt;sup>1</sup> Proc. Roy. Soc., 138A, 514, 1932.

chain molecules in the small crystals are supposed to be in a square arrangement. If the theory were correct it would follow that the structures change from the hexagonal, or densest close packing, into the square packing as the substances melt.

Reasons are given which suggest that the simple interpretation of the diffraction halo put forward in Stewart's theory is not likely to be correct, and that neither the square nor the hexagonal packing is pre-

dominant in the liquid.

A beam of monochromatic X-rays when passing through a thin layer of liquid n-paraffin or a similar chain compound produces always one particularly strong interference ring. The width of this ring is practically independent of the chain length, except for very short chains, and the same holds for the intensity distribution, provided the temperature at which the observations are made are not far from the melting-points.

The conditions necessary to produce interference have been discussed by Debye,3 Ehrenfest,4 Zernicke and Prins.5 It is shown that if the liquid consists of complex molecules interference may arise in the molecule itself or in the assembly of the molecules as a whole. The two effects may therefore exist simultaneously.

X-ray measurements on paraffins in the solid state 6 show that there are two fundamental periods in the chain molecule which might give rise to interference: One period, 2.52 ÅU, is the distance between identically situated CH<sub>2</sub> groups, the other period lies between 1.54 and 2 ÅU, and is the nearest distance between two carbon atoms or CH, centres in the chain.

Measurements on a number of n-paraffins (range of 21 to 29 carbon atoms) show further that the distance of nearest approach of the chain axes is  $4.74 \pm 0.02$  ÅU for substances in the solid state, and close to the melting-points.

Stewart, who has made a series of measurements on liquid paraffins, finds that the spacing corresponding to the diffraction ring obtained with the liquids \* is 4.64 ÅU. This spacing is observed for the intensity maximum in the diffraction halo. The comparison between the figures suggests that the interference ring is produced by the arrangement of the chain molecules in the liquid, and has no relation to the periods in the molecule.

Before discussing the possibilities of molecular arrangement in the liquid, a brief account will be given of the structure of the solid just before it melts.

In the solid the chain axes are all parallel to one another (the description refers to a single crystal). The intersection of the chain axes with a plane normal to their direction consists of a network of points. The experiment shows that these points are situated at the corners of equilateral triangles which cover the plane completely. Or, in other words, if the cross-section of the molecules were circles of diameter 4.74 ÅU, these circles would be arranged in a two-dimensional hexagonal close packing. The largest observed spacing of this network is  $4.74 \times \sqrt{3/4} = 4.11 \text{ ÅU}$ .

When the substances pass from the solid to the liquid state the density changes. The average volume of the molecules increases. This increase must be due chiefly to lateral expansion. The chemical binding

<sup>&</sup>lt;sup>3</sup> Ann. Physik, 46, 809, 1915; and Physik. Z., 2, 135, 1927.

<sup>&</sup>lt;sup>3</sup> Ann. Physik, 40, 609, 1915, 4 Proc. Roy. Soc. Amsterdam, 17, 1184, 1915. 6 Proc. Roy. Soc., 120, 437, 1928.

<sup>&</sup>lt;sup>7</sup> Physic. Rev., 31, 174; and 32, 151, 1928. \* Similar values have been found by Sogani and others.

of the  $\mathrm{CH_2}$  groups in the direction of the chain axes is strong, and the length of the molecule is not likely to be affected by the transition from the solid to the liquid. The density of the liquid at the melting-point is 0.78. The length of the chains, i.e., more precisely the long spacing of the substances in the crystals as obtained from X-ray measurements is found to be  $1.253 \times n + 2.3 \,\mathrm{ÅU}$  ( $n = \mathrm{number}$  of carbon atoms in the molecule). The average cross-section of a molecule is therefore between 22.0 and  $22.5 \times 10^{-16}$  sq. cm. for the substances dealt with here.

The chains behave as if they had cylindrical symmetry when the substances approach the melting-points. It is not likely that the symmetry should be less in the liquid. There are two ways in which cylinders may be close packed. One in which the axes go through the corners of equilateral triangles, the other in which they go through the corners of squares. These are the two arrangements which are likely to be found if the liquid preserves a crystalline state. If S is the cross-section area per molecule, then the largest observable spacing is:

 $\sqrt{\frac{S}{2}}\sqrt{3}$  for the triangular arrangement,  $\sqrt{S}$  for the square arrangement.

and

With  $S=22\times 10^{-16}$  sq. cm. the spacings are 4.36 and 4.70 ÅU. The observed spacing for the diffraction ring is 4.64 ÅU. If the assumption with regard to the crystalline state of the liquid is correct, it would appear as if the chain molecules in the liquid were in the square arrangement. Stewart regards this numerical agreement as a significant fact, and a support for his theory according to which the liquid is in a "cybotactic" state. If the hypothesis of the semi-crystalline liquid were true, it would follow that these substances when passing from the solid to the liquid form change from the triangular (densest) to the square packing.

It is, however, quite obvious that the agreement between observed and calculated spacing is no sufficient proof for the existence of the square arrangement. In order to make certain that this square packing really exists, it would be necessary to show that no other space-time statistical arrangement could give the particular diffraction ring observed with these chain compounds. Debye has shown that a limiting value for the distance of nearest approach is sufficient to produce a diffraction maximum. His theory cannot be applied quantitatively to the present case, but it seems obvious that his general argument must also apply to liquids.

This diffraction ring has considerable width, and covers, according to Stewart's measurements, a range between 3.8 and 5.8 ÅU. (The width is measured by the two angles at each side of the maximum for which the observed intensity drops to half the maximum value.) The calculated spacings corresponding to the triangular and the square packing are 4.3 and 4.7 ÅU, *i.e.*, well inside the width of the diffraction ring.

Zernicke and Prins 5 have pointed out very clearly that the interpretation of a diffraction ring necessarily involves the intermolecular forces in

the liquid. These forces are still entirely unknown in this case.

There is another aspect of the problem. The calculation of the average cross-section of the molecule does not take into account the statistical density fluctuations in the liquid. According to Stewart's theory, X-ray diffraction is produced by crystal aggregates of definite spacings. The width of the diffraction ring suggests that these aggre-

gates must be very small. The density variations of a very small volume in the liquid may be quite appreciable. Until this problem is discussed numerically no weight can be given to the numerical agreement under discussion.

It must further be remembered that although the chain molecule seems to have cylindrical symmetry that the scattering mass is not concentrated in the chain axis. This introduces a further difficulty in a quantitative treatment of the problem.

It therefore appears that all that can be safely said is, that the strong diffraction ring observed with these chain compounds is produced by the assembly of the molecules in the liquid, and that the average distance of nearest approach at a temperature not far from the melting-point is between  $4\frac{1}{2}$  and 5 ÅU.

# ANISOTROPIC MELTS: A STUDY IN CHANGE OF STATE.

By F. I. G. RAWLINS (Cambridge).

Received 13th Fanuary, 1933.

In a previous note, the present writer has referred to the analogy between the existence of two or more crystalline forms of the same chemical substance (polymorphy), and the change in co-ordination number (C. N.)—in Goldschmidt's sense—usually associated with fusion. In the latter process, (C. N.) usually decreases, at least for typical salts, which is but the reverse method of stating Lowry's concept of solidification by polymerisation.

In liquid crystals it is not unreasonable to think of the smectic stasis (that at lower temperatures) and the nematic stasis (that at higher temperatures) as akin both to polymorphy, with its associated temperature of transition between the two or more forms, and to change of state, also with its characteristic temperature of fusion.

There seems good reason to suppose that liquid crystals do not constitute a class by themselves, but that many more substances than are at present known in these forms should be capable of existing in such stases. The complicated phenomena shown by bismuth in the immediate neighbourhood of its melting-point suggest that a series of phases are involved, each having but an exceedingly narrow range of temperature, and differentiated by marked discontinuities in magnetic properties. The crystal structure of bismuth points to the possibility of films or sheet forms, such as are needed for the smectic stasis.

For a discussion of the conservation of molecular units through a change of state, it is clearly important to know from which actual form of the solid the gaseous molecules or atoms are liberated—for example, in the act of sublimation. Thus one comes to regard the liquid-crystalline condition as the theoretically-likely condition of matter immediately below the point of fusion. That the majority of substances up to the present recognised as capable of existing in this form are

complicated carbon compounds may be a mere accident, depending in some way upon the molecular rigidity of the long chain molecules, whether zig-zag or straight.

The process of sublimination is thus unique in forming (on the view expressed above) the passage from a state or states in which molecular birefringence co-exists with structural birefringence, to a

state possessing molecular birefringence alone.

There is good reason for thinking that a considerable degree of (statistical) co-ordination exists in many true liquids: 2 this, however, probably approximates as a whole to something approaching a cubic distribution, which would render such phases structurally isotropic, though by no means necessarily so in the more ultimate sense already suggested. The questions for future experiment to decide arise naturally out of what has been said above.

Firstly, an enquiry into the structural anisotropy of liquid-crystal-line phases. Our information as yet is almost wholly from X-ray and magnetic data. The former is naturally incapable of shedding light upon the dynamical behaviour of the "regiments" (Stewart) composing the stases under consideration. To this end, observations in the infra-red are indicated. Their purpose would be (a) to confirm in liquid crystals the "internal" oscillations of certain carbon groups (already well-known under other circumstances), and (b) to stimulate the "external" frequencies, i.e., those connected with the movements of Stewart's "regiments" as a whole, in contra-distinction to the vibrations of the units composing them. The problem of the nature of the linkages would be a stage nearer solution, as well as offering a check upon X-ray structures.

By working with polarised radiation, most of the vectorial properties could be determined. Actually, owing to the high molecular weight of the complexes, the "external" spectrum would be a long way out in the far infra-red, but recent technique has brought that region within the scope of moderately refined experimentation. Some observations upon the power of infra-red studies upon azoxianisol are due to G.

Laski.3

The second matter needing consideration is a systematic attack upon the optical properties of a large number of carefully selected anisotropic melts in the visible spectrum. Such investigations (as indeed those in the infra-red also) would derive increased value from being conducted over appropriate ranges of temperature, the importance of which has been stressed by several workers on the present occasion.

It is not the individual properties of these liquid crystals and anisotropic melts, fascinating as they are, which merit attention so much as the recognition that the smectic and nematic stases may prove to be states of matter of wide significance, providing new clues to molecular structure and in consequence of great interest both to crystallographers and to chemists.

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    Cf. Mark , loc. cit., p. 410.
    Laski, Erg. exakt. Naturw., 3, 112, 1924.
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# THE STUDY OF CRYSTALLINE ORIENTATION BY ELECTRON DIFFRACTION.

By J. J. TRILLAT (Besançon).

Received in French, 1st March, 1933, translated by H. D. Megaw.

The phenomena of the orientation of crystals and molecules have been studied for many years by a large number of workers. The interest taken in these researches is justified by the importance of the results and by the advances which they have made possible in our knowledge of the different structures of matter.

It is now known that many fundamental phenomena, in physics as well as in chemistry and biology, are directly due to the orientation of molecules or crystals. Among these, for example, are adsorption, birefringence, magnetic properties, mechanical properties, and even in certain cases chemical properties of surface layers. Hence it is particularly important to be able to use methods which give exact information about the way in which the molecules and crystals are arranged.

These methods may be divided into the following groups: those involving the optical phenomena of birefringence, which are used in particular for the study of crystals and mesomorphous substances; those which employ electric or magnetic properties; those dealing with the study of very thin films, such as those formed on the surface of water or mercury; and finally, those involving the use of X-rays.

For some years, following immediately from the fundamental discoveries of Louis de Broglie, a new method of investigation has been available; this is *electron diffraction*, otherwise referred to as "*electron analysis*." It consists in sending a fine beam of electrons of uniform energy through a thin layer of a substance, or on to the surface of any substance; the waves associated with the electrons are diffracted, and give rise, in certain cases, to beautiful interference phenomena of great intensity.

It might be thought that the diffraction of electrons would give the same information as that of X-rays. This is sometimes true, but on the other hand there is a large range of phenomena which is peculiar to the electrons.

In fact, X-ray spectrography differs from that using electrons in several important points. The first of these is that the experimental technique is different, and involves working in a high vacuum. A further and fundamental difference is that the X-rays can penetrate considerable thicknesses of material, thus giving photographs which may be considered as representing an average state; while the electrons, being heavily absorbed, make possible the study of extremely thin layers, which are sometimes only a few molecules thick. Owing to this fundamental property, a much finer analysis can be made by the use of electrons. Thus it is possible to study the surface of a body, to find the structure of monomolecular layers or layers only a few molecules thick, and to show the existence of single crystals of very small dimensions.

It is essential that the work should be done with well-defined experimental conditions, as, for example, that the beam of homogeneous electrons should be as narrow as possible.

The method of electron analysis has another advantage, that it requires very small quantities of the substances investigated, and very low potentials; with ordinary conditions, a few watts will give diffraction effects which can be seen on a fluorescent screen, and which can be

recorded in a fraction of a second on a photographic plate.

I do not propose in this article to give an account of all the applications of electron diffraction.¹ I shall deal only with those which throw light on the orientation of molecules or crystals; I shall investigate first the case of perfectly crystallised solids, such as metals, then the case of imperfectly crystallised substances, such as certain organic compounds, and finally the case of liquids, which have hitherto hardly been studied by this method.

# 1. Crystalline Orientation of Metals.

It has been known for many years that the crystals which compose metals readily orient themselves in a particular way under the influence of mechanical treatment. These researches have been brought to a high degree of perfection by the use of X-rays; they have proved the existence of fibrous structures, characteristic of each metal or group of metals, and also characteristic of the mechanical treatment. The crystallographic directions or planes, along which orientation occurs in any given case, are known; the structures due to rolling, drawing, and hammering are directly related to the mechanical properties of the metals, and can be modified by heat treatment. The use of X-rays, which makes possible the complete theoretical study of these phenomena, is thus of considerable interest.

By means of electron analysis, these investigations can be completed,

and in certain cases new results obtained.

By sending a narrow beam of homogeneous electrons through a very thin film of aluminium prepared by rolling, G. P. Thomson <sup>1</sup> was able to show the effect of orientation due to this mechanical treatment. More recently, J. J. Trillat and Th. von Hirsch <sup>2</sup> have examined films about  $50\mu\mu$  thick obtained by hammering, using homogeneous electrons of about 40 to 50 KV; the apparatus is shown in Fig. 1, and also in Plate I. By this means we have been able to show that a film of beaten gold has a fibrous structure, one axis [100] of the cubic face-centred crystal being always oriented perpendicular to the surface of the film.

We have also been able to show the existence of plastically deformed single crystals oriented in the same way; some examples are given in Plate I., Figs. 2 and 3. I shall not deal here with the question of detailed theoretical interpretation, as this has been given in other papers (see Bibliography). One of the interesting features of this method is that it makes it possible to investigate the metallic film at every point; brilliant interference figures appear on the fluorescent screen which represent the

structure at each point.

When these films are heated, at first there is a decrease in the deformation of the crystals; then at a certain temperature recrystallisation sets in, and the orientation disappears completely (Plate I., Fig. 4).

It is thus possible to follow, at every point, the effect of thermal treatment on the structure of the metal, and to do so almost instantaneously.

## PLATE I.

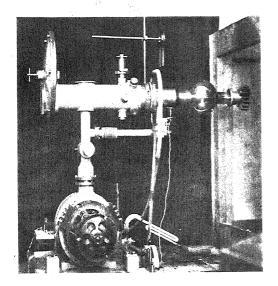


Fig. 1.—Apparatus for diffraction of electrons (J. J. Trillat).

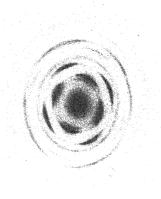


Fig. 2.—Leaf of beaten gold. Single crystal plastically deformed. (Electrons of 40 KV.)



Fro. 3.—Beaten gold. Single crystal plastically deformed.



Fig. 4.—Leaf of beaten gold heated 2 hours at 240° C.

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#### PLATE II.

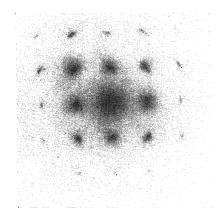


Fig. 5.—Leaf of beaten platinum. Single crystal, orientation [ror]. (Electrons of 40 KV.)

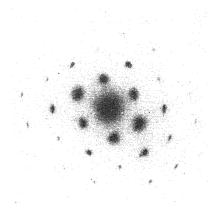


Fig. 6.—Leaf of beaten platinum. Single crystal, orientation [110].

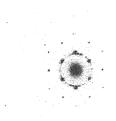


Fig. 7.—Paraffin. Single crystal. (Electrons of 40 KV.)



Fig. 8.—Stearic acid α.

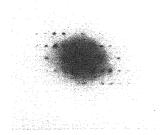


Fig. 9.—Stearic acid  $\beta$ .

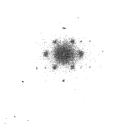


Fig. 10.—Stearic acid  $\gamma$ .

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For this purpose I am having a small oven made, by means of which I can study the phenomena at every instant, always on the same crystal;

in fact, the method is actually a cinematographic analysis.

Films of silver, aluminium, copper, platinum, etc., were studied in the same way from the point of view of their crystalline orientation. In the case of beaten platinum, the photographs are particularly sharp, and show the existence of single crystals which are very little deformed, and are oriented with either a [100] or a [110] axis perpendicular to the surface of the film (Plate II., Figs. 5 and 6).

Many other investigations may be made by means of electron analysis. One of the most interesting concerns the orientation of metal crystals deposited by sputtering. Whether orientation does or does not occur depends on what gas is used in the sputtering apparatus, and its pressure; as well as on the nature of the substance on which the deposit is made (mica, celluloid, NaCl, etc.). It sometimes happens that the metal

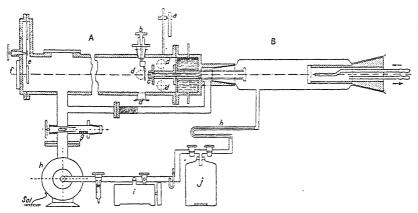


Fig. 1.—Apparatus for diffraction of electrons. A. Anodic part. B. Cathodic part. (a) Magnetic. (b) Pivoted support for preparation. (c) Collimator cooled by water chamber. (d) Pivots. (e) Plate carrier. (f) Lead glass window. (g) Dessicant. (h) Holweck molecular pump. (i) Oil pump. (j) Receiver for passing air through capillary K when the apparatus functions as a gas tube.

crystallises in a particular form; thus, G. P. Thomson showed that nickel, deposited in an atmosphere of argon, was always hexagonal. The orientation of electrolytic deposits can be observed in the same way.

G. P. Thomson has also shown that it is possible to observe certain chemical reactions such as oxidation, even when they only occur to a very small extent. Thus, a sheet of polished copper which has been exposed to the air for three-quarters of an hour is sufficiently tarnished to give rings which can be detected, even though the brilliance of the surface appears to be quite unchanged; from the photograph, it is possible to show that oxidation has taken place, giving Cu<sub>2</sub>O.

The structure of layers of gas adsorbed at the surface of metals has been demonstrated by Davisson and Germer <sup>3</sup> from the reflection of slow electrons. The gas molecules are arranged on a kind of two-dimensional lattice on the surface of the metal. Other work of the same kind has been done by Rupp <sup>4</sup> and by Thomson, <sup>5</sup> in connection with the catalytic properties of metals.

## 2. Structure and Orientation of Various Thin Layers.

Electron interference is extremely useful for the investigation of the structure of thin crystalline layers. The methods are plainly not confined to metals, but can be used for many other substances, minerals and organic compounds, so long as it is possible to overcome the experimental difficulties, particularly that of obtaining sufficiently thin layers.

The solution of this difficulty varies with the particular case. general, it may be said that all substances of which the crystals form layers or sheets (mica, graphite, fats, etc.) are especially suitable for electron analysis, as are also those which give homogeneous films by the evaporation of solutions (celluloid, fats). From an examination of the structure of these films or surface layers it is thus possible to determine the orientation and arrangement of the molecules and crystals; and it is clear that this question is of great interest to the chemist as well as to the physicist.

Interesting work on the structure of thin crystalline layers has been done recently by F. Kirchner.<sup>6</sup> A systematic investigation of thin layers of about twenty different substances deposited on mica or celluloid has shown the existence of privileged orientation of the crystalline grains; this orientation occurs almost without exception when the layers are obtained by evaporation at atmospheric pressure (sublimation), and also in the majority of cases when the layers are obtained by evaporation in vacuo. The fibrous structure which is apparent from the photographs is characterised by the fact that a fixed plane of the lattice is oriented parallel to the plane of the support. The theoretical interpretation of these structures, like those dealt with above in connection with beaten metals, is particularly simple.

On the other hand, in the case when the thin layer is obtained by slow evaporation in vacuo, an increase in the width of the interference rings is always found to occur at the beginning to a greater or less extent; and this, as is known from the results of X-ray work, is characteristic of the colloidal state of the layer (extremely small grains). When the thickness of the layer and the velocity of evaporation increase, the size

of the grains generally increases also.

With certain crystals (for example, CdCl<sub>2</sub>) it is possible to follow the spontaneous transition, as a function of the time, from the random distribution which exists in the colloidal state to the perfect orientation of bigger crystals and finally to the oriented single crystal. The natural evolution of the structure of the layer can thus easily be observed and studied, from the point of view of both the size and the orientation of the crystals. This transformation does not merely involve a growth in size of the original crystals, but also a regular arrangement of crystals which initially were distributed absolutely at random.

Work of this kind has been done by Kirchner on thin layers of bismuth, gold, antimony, tellurium, as well as on CdCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, Sb<sub>2</sub>O<sub>3</sub>, NH<sub>4</sub>Cl, MgO, etc.

#### Structure of Charcoal.

It is well known that carbon in a finely divided state has the property of adsorbing gases, and is used for this purpose in very many cases. The amount of adsorption varies with the preparation of the charcoal and its state of division, and depends to a very great extent on its structure; the X-ray diagrams show sometimes an amorphous state, sometimes a

semi-crystalline state, and sometimes a crystalline state (G. L. Clark). Investigation with electrons can throw new light on these questions.

When a linear diaphragm with silver edges was passed very rapidly through a sooty flame, Ponte? observed an intense blackening of the photographic plate; superimposed on this were several faint rings, of which the diameters corresponded to lattice spacings identical with those of graphite. From this it appears that soot consists of graphite in the form of very small crystals (indistinct rings), while the particles give rise to a general diffusion of the electrons.

More recently, F. Trendelenburg <sup>8</sup> repeated this work. He deposited "Russ" charcoal on a very thin leaf of celluloid or gold, and obtained on the photographic plate a complete system of Debye-Scherrer rings of uniform intensity, due to the graphite. It is noteworthy that X-ray analysis of this "Russ" charcoal shows nothing, on account of the excessive smallness of the crystals; investigation by electrons, on the other hand, makes it possible to prove that the structure is not amorphous, but that crystals exist of the order of 50 Å in size.

## Organic Films: Fatty Acids and Paraffins.

It is natural to try and extend the possibilities of electron analysis to films consisting of long-chain organic molecules, such as fatty acids, triglycerides, or saturated hydrocarbons. By means of the large amount of X-ray work done on these substances, their molecular and crystalline structure has been determined, and it has been shown that orientation of the carbon chains occurs at the surface of contact with different substances (glass, metal, water) (J. J. Trillat <sup>9</sup>).

As it is comparatively easy to prepare extremely thin films of these substances, it is probable that electron diffraction can give new information about these phenomena, which are likely to be of increasing interest as the number of molecules in the thickness of the layer becomes less (a film of stearic acid  $40\mu\mu$  thick consists of 10 molecular layers).

For this purpose, J. J. Trillat and Th. von Hirsch <sup>10</sup> have used films of stearic acid and the corresponding hydrocarbon obtained by letting dilute benzine solutions of the substances evaporate on the surface of water. A narrow beam of homogeneous electrons of 40 KV. ( $\lambda = .06$  Å) is sent through the film; the film can be moved parallel to itself, and thus can be investigated at every point.

The paraffin (orthorhombic crystals) in general gave a diagram consisting of Debye-Scherrer rings; by turning the preparation about an axis normal to the electron beam, it can be shown that the crystals are oriented by the water in such a way that the basal plane (ab) rests on the liquid, the carbon chains thus arranging themselves normal to the surface. The explanation of this phenomenon, which was previously observed by the author by X-ray methods, has been given in other papers. In certain cases, however, the paraffin crystallises in large single crystals, which are very well formed and perfectly oriented. The diagrams then consist of very sharp diffracted spots (see Plate II., Fig. 7), which are given by all the planes of the zone [001] (indices hko); the arrangement of spots is simply the reciprocal figure of the lattice plane parallel to the surface of the film. It is very easy to allot the appropriate indices to each spot, and to calculate directly the lengths of the edges forming the base of the orthorhombic prism.

Stearic acid (monoclinic crystals) orients itself on water so that the

carbon chains lie *obliquely* relative to the surface of the liquid, the endgroup — COOH being in contact with the surface. Investigation of these films gives diagrams of a different type (Plate II., Figs. 8, 9, 10). Without going into detail, we may say that they correspond to different polymorphic forms,  $\alpha$ ,  $\beta$ ,  $\gamma$ , which are thus at once identified, and from which it is possible to determine the parameters of the basal plane of the monoclinic prisms.

#### Films of Nitrocellulose.

The remarkable successes achieved by X-ray spectrography in dealing with the constitution of highly polymerised substances occurring in nature (gelatine, indiarubber, cellulose, etc.) have suggested to several experimenters that electron diffraction might also be applied to this problem.

The first results of this sort were obtained by G. P. Thomson and Reid. They showed that very thin sheets of celluloid gave three diffuse rings resembling those given by celluloid with X-rays, and suggesting a structure akin to that of a liquid, with intermolecular distances of 3.6 and 4.3 Å.

More recently Kirchner, 12 who likewise used very thin sheets of celluloid and nitrocellulose, obtained very characteristic diagrams consisting either of well-defined concentric rings or of points. In the latter case, the figure (Plate II.) is due to a single crystal acting as a two-dimensional lattice. When the X-ray results are taken into account, the diffraction of the electrons must be attributed to crystals of nitrocellulose, formed by the action of elastic stresses, and too small to be revealed by X-rays. It is not yet possible to say anything about the chemical composition and complete structure of these crystals, but it is to be hoped that interpretation of the photographs will lead to an increase in our knowledge of these cellulose derivatives.

These phenomena of crystallisation, which I have investigated on different occasions by other methods, <sup>13</sup> are a function of the time of drying of the film, and only appear when the films are old.

The results obtained by Dauvillier, <sup>14</sup> are not in complete agreement with those given above. He used films of nitrocellulose about 100 Å thick, which he prepared by evaporation from solution on the surface of water or mercury. The photographs generally consist of several diffuse rings, and resemble those found by G. P. Thomson (*loc. cit.*). In one case, however, Dauvillier obtained a photograph consisting of spots arranged in a hexagonal pattern, which were certainly due to a fairly large single crystal. This is explained by him by the supposition that the cellulose chains are oriented perpendicular to the plane of the film, and that they are regularly distributed at the corners of a hexagonal net. The ordinary structure of cellulose films is the same, except that the area of the microcrystals is very small compared with that of the cathode beam (O·OI mm.²) and that they are oriented at random about their long axis.

The experimental fact that the thick films (10 - 5 cm.) obtained on mercury are impermeable to gases, while those prepared on water are not, is probably due to a difference in the amount of orientation in the interior of these thick films.

Taylor Jones, 15 using thin films of celluloid, has also obtained photographs consisting of rings or spots; and he suggests an arrangement of the molecules in which each hexagonal group is considered as having

six diffracting centres situated at the corners of regular hexagons, all the hexagons being arranged in layers parallel to the surface of the film.

These results show the use of electron analysis in investigating colloidal and fibrous substances. X-ray analysis, which has chiefly been limited to the study of fibre photographs, because of the difficulty of obtaining big enough crystals of cellulose, can thus only determine in an approximate way the crystal system of cellulose and its derivatives; but electron analysis, which can deal with single crystals, should make it possible to complete our knowledge of these substances. Similarly, it should also make it possible to study the factors which govern the orientation of molecules or micelles.

## 3. Surface Structure of Liquids.

The surface of a liquid, which is marked by a discontinuity in the molecular field, has been studied by several investigators, but only by surface tension, optical or X-ray methods. This work suggests that the surface layer of a liquid has not the same structure as a layer in the interior of the same liquid; it has a greater resemblance to the crystalline state, or rather, to a state oriented in a statistical way. Of course, this depends to a large extent on the structure of the molecules. It is an interesting problem, for it directly concerns our knowledge of the liquid state, and also the phenomena of adsorption and surface tension.

In connection with this, I previously examined the free surface of a number of organic liquids with long carbon chains, using the method of the tangential drop (J. J. Trillat <sup>16</sup>); I showed that this surface certainly consists of molecules oriented perpendicular to the surface, subject at the same time to a certain amount of agitation. The free surface somewhat resembles a mesomorphous state, where the molecules have simply an average orientation, without being fixed in a crystalline lattice.

Some experiments have been made using homogeneous electrons reflected from the surface of liquids; the point of this method is that the electrons, being very little absorbed, give a direct image of layers which are wholly on the surface. Thus Rupp and Buhl <sup>17</sup> showed, by the reflection of slow electrons, that the free surface of various mineral oils consist of oriented molecules; the mean length of the molecules is thus determined. These results confirm those which we have obtained with X-rays.

Recently, Wierl <sup>18</sup> has investigated the diffraction of fast electrons (50 KV.) at the free surface of mercury. He claims to have found sharp diffraction rings corresponding to a *perfectly defined crystalline structure*. Precautions were, of course, taken to avoid the presence of solid impurities, such as mercuric oxide, on the surface.

I attempted to repeat these results, using perfectly clean mercury surfaces. The metal was placed in a small support, and a very narrow, intense beam of electrons impinged on it almost tangentially. In spite of rather long times of exposure, I could never obtain diffraction rings, but only a general blackening of the film. I consider that the rings observed by Wierl must be due to some cause other than surface "crystallisation," which would be a very surprising phenomenon if it did occur.

This negative result should not, however, prevent the research from continuing. It seems, indeed, that electrons may provide a very powerful method of studying the surface of liquids, and also the mesormorphous phases which occur in certain substances. We intend to continue work

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in this direction, and also to examine substances which show a state intermediate between the crystalline and liquid states.

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## ANOMALOUS VISCOSITY IN MESOMORPHIC MELTS.

By Wolfgang Ostwald (Leipzig).

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Twenty years ago, the author, in these *Transactions*, called attention

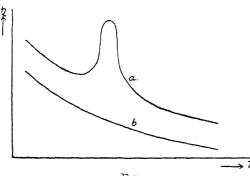


FIG. I.

to the fact that systems of very different natures show anomalies of the same kind in the variation of their viscosity with temperature. As a rule the viscosity of liquid systems tends to increase steadily with decreasing temperature, and vice versa. But certain substances behave otherwise; for example, albumen sol, starch sol, liquid mix-

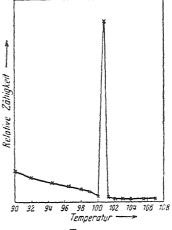
tures of critical concentration, molten sulphur, and, last but not least,

<sup>1</sup> Trans. Faraday Soc., 4, 1913.

a large number of mesomorphic melts. These substances show an anomalous viscosity represented by the upper curve in Fig. 1. Instead of a regular increase in the viscosity as the temperature decreases, we find a sharp maximum at a certain point. This type of curve, known as the viscosity curve of colloidal segregating mixtures, occurs in cases where a homogeneous or finely dispersed system separates into a heterogeneous or coarsely dispersed system, if the essential condition is fulfilled

that during the separation a distinct colloidal state occurs as an intermediate stage. For example, if viscosity measurements are made on the system phenol-water in concentrations other than the critical one, where the colloidal opalescent transition stage is very much reduced, and a coarsely dispersed emulsion at once occurs, then the ordinary simple curve shown in b, Fig. 1 is obtained.

The fact was mentioned that these anomalous viscosities are obtained with certain mesomorphic melts. An excellent new example of this is shown in Fig. 2, which represents the curve obtained by D. Vorländer 2 for the ethyl ester of cholesteryl carbonic acid. Measurements made on other cholesteryl esters gave similar results.



The occurrence of viscosity curves of segregating mixtures for mesomorphic melts is an important piece of evidence, though not the only one, for the theory suggested long ago, 3 that certain mesomorphic melts show a state of dispersion which is typical of colloids. The details of this may be found in a paper published some time ago by the author summarising the relationships between mesomorphic and colloidal systems.4

2.

In the interesting discussion on "Colloids and their Viscosity," organised twenty years ago by the Faraday Society, attention was called for the first time by the chairman, Mr. Hatschek, to the importance of a second anomaly in the viscosity. The viscosity of solvated colloids (and certain coarser suspensions, emulsions, and foams) varies with the rate of shear. The Hagen-Poiseuille law does not hold for these systems. The velocity of flow in a capillary is not proportional to the pressure, but is disproportionately small for small pressures. Such systems (e.g., a gelatine or rubber sol) seem to have very much higher viscosities for small velocities than for large. This anomaly has so far been found only in colloids and certain more coarsely dispersed systems. If it should be found in molecularly dispersed systems, it would be much smaller, of quite a different order of magnitude. Thus the occurrence of large anomalous viscosity, the so-called "structural viscosity," can be

D. Vorländer, Z. Krist., 79, 78, 1931.
 Wo. Ostwald, Koll. Z., 8, 270, 1911; Th. Svedberg, Koll. Z., 16, 103, 1915. <sup>4</sup> W. Ostwald, Z. Krist., 79, 222, 1931.

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considered, according to the experimental results hitherto obtained, as evidence for the existence of a super-molecular or colloidal discontinuity.

The question next arises whether mesomorphic melts show this anomalous viscosity also. If it were found to occur, it would be a further proof of the close relationship existing between certain mesomorphic melts and colloidal systems.

3.

It has been shown experimentally by the author and Mr. H. Malss that mesomorphic melts of ethyl p-azoxybenzoate, cholesteryl acetate, propionate, and butyrate give these anomalies typical of colloids to a very marked extent.

Figs. 3 and 4 are examples selected from a more extensive series of measurements. They refer to ethyl p-azoxybenzoate and cholesteryl propionate respectively, two substances which are chemically completely different. The pressure is taken along the X-axis, the relative viscosity along the Y-axis. The temperature is constant for all points on the

It is apparent that for high temperatures, above that for which the viscosity is a maximum (isotropic melts), the viscosity is independent of the pressure;

the horizontal straight lines show that the Hagen-Poisuille law holds even for the In the region where lowest pressures. anisotropic melts occur, however, relative viscosity increases enormously with decreasing pressure. Here we find structural viscosity in its extreme form.

With reference to the experimental method, it may be remarked that we worked with a Tsuda viscometer,5 which, as a test, was used to determine the absolute as well as the relative viscosities of water and glycerine. The measurements were not easy on account of the high temperature coefficient in this range. substances used were not bought synthesised by ourselves, purified and

recrystallised, the meltingpoint defined.

It may be of interest in this connection that closely similar curves are given by mixtures of liquids in concentrations 6 critical

160 150 same curve. 140 130 120 110 100 95 90 85 80 75 70 65 60 55 50 45/1 40 35 30 25 F1G. 3. <sup>5</sup> S. Tsuda, Koll. Z., 45, 325, 1928. mental Biology), 9, 83, 1932.

<sup>&</sup>lt;sup>6</sup> Wo. Ostwald, The Robertson Memorial Volume (Australian Journal of Experi-

(hexane-nitro-benzene, hexane-methyl alcohol, isobutyric acid-water, phenol - water, phenol-heptane, benzene - acetic acid-water) as well as molten 500 sulphur, bees-480 wax, etc.; but not by melts 460 οf dextrose (heated for 440 short time), lauric and 420 stearic acids, benzophenone, 400 naphthalene, The oc-380 currence of structural vis-360 cosity in melts is therefore 340 essentially neither frequent 320 nor unspecific. 300 Summary. وا 280 Mesomorphic melts of ethyl 260  $\phi$  - azoxybenzoate, cholestervl acetate, butyrate and propionate, in the ranges in which 200 they are anisotropic, show 180 marked very structural vis-160 L cosity; in other words, they do 140 not obey the Hagen-Poiseuille 120 law connecting viscosity with 100 rate of shear. In this region, therefore, as far 80 as their viscosity 70 is concerned they behave like 50 711.5° gelatine or rub-40 ber sols. This is further proof of 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 the close rela-FIG. 4. tionship

exists between colloids and (certain) mesomorphic systems.

# A REMARK CONCERNING THE VISCOSITY OF LIQUID CRYSTALS.

By R. O. Herzog and H. Kudar.

Recently a kinetic theory of the viscosity of liquids, which is based on the following considerations, has been developed.<sup>1</sup>

The experimentally determined viscosity of polyatomic liquids can be traced back to the translational and rotational motions of the molecules. The part of the viscosity which results from the *translational* motion of the molecules is given for approximately spherical molecules by the formula

$$\eta_{\text{trans.}} = \frac{1}{3} \sqrt{\frac{8RT_e}{\pi M}} \cdot \frac{r}{v - \omega},$$

where  $T_e$  is the melting-point,

M molecular weight,

v specific volume.

 $\omega$  Batschinski's effective volume, defined by  $\omega$  .  $M=b_e,$  the Van der Waals' volume constant at the melting-point.

$$r$$
 molecular radius, calculated from  $\frac{\omega M}{N} = \frac{4\pi}{3}r^3$ .

The formula is closely related to that which Jäger derived on theoretical grounds, and also to Batschinski's empirical formula  $\left(\eta = \frac{\mathcal{C}_{\mathrm{B}}}{v - \omega}\right)$  where  $\mathcal{C}_{\mathrm{B}}$  is a constant characteristic of the substance.

One finds the rôle played by molecular *rotation* in viscosity by assuming that from the point of view of hydrodynamics the molecules behave as macroscopic bodies. The experimentally determined viscosity is found to be given by the formula

$$\eta_{\text{exp.}} = \eta_{\text{trans.}} \left( \mathbf{I} + \frac{\eta_{\text{rot.}}}{\eta_{\text{trans.}}} \right) = \eta_{\text{trans.}} \left( \mathbf{I} + x \cdot \frac{r}{\rho} \right),$$

where for  $\eta_{\text{trans.}}$  the above value is to be substituted and x is a factor which depends on the distribution of mass in the molecule.  $\rho$  is the mean value (for all directions of the axes) of the ratio

$$\frac{\text{Moment of inertia}}{\text{Linear axial moment}} = \frac{\Sigma m_i r_i^2}{\Sigma m_i r_i},$$

where the  $m_i$  are the masses of the individual atoms and the  $r_i$  are the distances from the axes of rotation.

For rod-shaped molecules—according to Vorländer liquid crystals have this form—r in the formula for  $\eta_{\text{trans.}}$  is taken as half the length of the rod. For  $x \cdot r/p$  a complicated expression computed from the molecular dimensions and the position of the atoms in the molecule is to be substituted. The interatomic distances are taken either from Bragg's X-ray determinations or from other known sources.

The assumption of the calculation is that, because of the cybotactic influence (Stewart) only rotations about the long axis are possible in addition to the translational motion, so that only these rotations are to be taken into account hydrodynamically.<sup>2</sup> In this case the axis of rotation is the line through the centre of gravity of the molecule; characterised by the requirement that the sum  $\Sigma m_i r_i$  be a minimum.

Although the theory has been derived for dipole-free substances, one may investigate whether similar considerations may not apply to liquid crystals, even though these have dipole moments. Though the experimental data are quite incomplete a survey of them from this point of view is indicated for the reason that there seem to be cases for which Batschinski's formula, that is, a linear relation between the specific volume and the fluidity, holds (for example, p-ethyoxybenzalamino- $\alpha$ -ethylmethylcinnamate and p-anisalazophenolethylcarbonate).

TABLE.

$p$ =Ethoxybenzalamino-α-ethyl methyl cinnamate.  Isotropic ( $ω_J = 0.923$ ).		$p$ =Anisal azophenol ethyl carbonate. $Isotropic (\omega_{\rm J} = 0.9565).$	
121·0 123·6 127·6 132·3 138·2	2·49 2·46 2·48 2·49 2·55	115·0 124·5 130·6 136·8 141·2	2·II 2·I0 2·09 2·09 2·26
Anisotropic ( $\omega_{\Lambda} = 0.907$ ).		Anisotropic ( $\omega_{\Lambda} = 0.9398$ ).	
t.	$\eta(v-\omega_{\rm A})$ , 10 <sup>5</sup> .	t.	$\eta(v-\omega_{\mathrm{A}})$ . 103.
76·0 86·3 96·0 105·0 112·5 118·7	2·93 2·95 3·02 3·02 2·93 2·85	99·5 104·0 110·0	2·99 3·00 3·02 3·07

The values for  $\eta(v-\omega)$  are found to be *smaller* for the amorphous phase than for the anisotropic phase;  $\omega_A < \omega_J$ . If  $[\eta(v-\omega)]$  differs little for two neighbouring phases, one may conclude that the phases differ little from the molecular-kinetic point of view.

<sup>2</sup> For example, for the paraffins, the formula turns out to be

$$\eta_{\rm exp.} = \eta_{\rm trans.} \left( {\rm i} \, + a/\delta \, . \, \frac{{\rm i}}{\frac{4}{\ln c/a + {\rm i} \cdot {\rm i} {\rm 93}} + \frac{{\rm i}}{\ln c/a + {\rm o} \cdot {\rm i} {\rm 93}}} \right), \label{eq:exp.}$$

where c is half the rod length and a the radius of the rod considered as a cylinder.

The case of p-ethoxybenzalamino- $\alpha$ -ethyl methyl cinnamate merits further discussion. (2c  $\sim$  21Å.; a=2.67Å from  $\frac{\omega_{\text{A}} \cdot M}{N}=2c \cdot a^2\pi$ ).

$$\frac{C_{\rm B}}{\eta_{\rm trans.}(v-\omega_{\rm A})}-1=2.95.$$

By combination with

$$\frac{a}{\delta} \cdot \frac{1}{\frac{4}{\ln c/a + 1 \cdot 193} + \frac{1}{\ln c/a + 0 \cdot 193}} = \frac{1 \cdot 23}{\delta}$$

one finds

$$\delta = \frac{1.23}{2.95} = 0.42 \text{Å}.$$

This small value <sup>3</sup> cannot be explained on stereochemical grounds even when most of the atoms are assumed to be close to the axis of rotation. Accordingly, the excess viscosity over that calculated on the basis of the mechanical model must be attributed essentially to the damping action of the dipole moments.

 $^3$  For the paraffins one finds o 765Å. If the distance is calculated in the same way for stearic acid considered as bimolecular (between its melting-point and 80°, from the study of W. Herz) one finds

$$\frac{C_{\rm B}}{\eta_{\rm trans.}(v-\omega)} - {\rm i} = 2.5{\rm i}$$

for

$$\frac{a}{\delta} \cdot \frac{1}{\frac{4}{\ln c/a + 1 \cdot 193} + \frac{1}{\ln c/a + 0 \cdot 193}} = 2 \cdot 24,$$

an approximate agreement.

#### LYOTROPIC MESOMORPHISM.

By A. S. C. LAWRENCE (Department of Colloid Science, Cambridge).

Received 30th Fanuary, 1933.

It is interesting to recall that Lehmann's liquid crystals of ammonium oleate, which formed the foundation of the subject under discussion, were deposited from solution; and also that the amount of water present profoundly modified their form. Since that time, however, most of the substances studied have been in the form of anisotropic melts of single compounds. The action of heat and of a solvent are not dissimilar insofar as they both loosen the directive forces holding the molecules in their normal crystal lattice. For a mesoform to appear, it is necessary for these forces to persist in either one or two dimensions after loosening of the third. But even when this occurs and a mesoform exists it is unlikely that heat and all solvents will bring this about equally well.

In the following pages solutions, both colloidal and crystalloidal, are described to show that structures in liquids, although not always apparent

or highly organised, can be detected by their characteristic results. It is already known that some substances when containing water form mesophases similar to those of anisotropic melts. For example, bromphenanthrene-sulphonic acid; 1 but the solutions of this substance have not yet received attention. This also applies to other substances such as the soaps and the soap-like alkali salts of the naphthenic \* and resin acids.2 In crystalloidal and in colloidal solutions structure shows itself in different ways. In the former, structure may lead to the existence of a mesoform during crystallisation. As already indicated, the same thing occurs in colloids; but in their solutions, even when quite dilute, there is a structure which distinguishes them sharply from normal liquids. There are, too, colloidal solutions possessing structure but without any other sign of mesoform. Benzopurpurin is an example.3

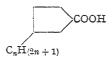
It has been suggested that there is a connection between colloids and crystalloids in the soaps since they are colloids and also exist in mesoforms.4 However, soaps are just as much crystalloidal as colloidal and the mesoforms upon which the suggestion is based are the crystalloidal ones in which there is no evidence of colloidal dispersion at all. The real colloidal mesoforms of soap are very different from the orthodox ones. The two structures are not even built up from the same units and the degree of organisation in the structure of colloidal solutions is so different that special methods are required for its detection. The mesoforms will be discussed as follows:

- I. Crystalloidal mesoforms of soap,
  - (a) anhydrous,
  - (b) + water.
- 2. Anisotropic soap solutions—the true colloidal mesoform.
- Structure in crystalloidal solutions.

## Crystalloidal Mesoforms of Anhydrous Soap.

Vorländer has observed mesoforms in the anhydrous sodium salts of the fatty acid series when heated to rather high temperatures.<sup>5</sup> Fig. I gives his results for the transition temperatures to the mesoform and the melting-points to isotropic liquid, plotted against chain length (as number of carbon atoms). The irregularity of both sets of results is striking. Since this might be due to decomposition setting in or to traces of water, which is not easily removed completely from a soap, we have examined in this laboratory the ammonium salts of the fatty acids. These melt below 100° so that there is no decomposition if heated in sealed tubes; and also they can be prepared without any water ever being present, by passing dry ammonia gas either into a solution of the fatty acid, the solvent being distilled off afterwards in a sealed apparatus,

 $^{\rm 1}$  H. Sandquist, J.A.C.S., 40, 556, 1916. \* These are the higher alkyl homologues of methyl-cyclo-pentane-carboxylic acid of the general formula:



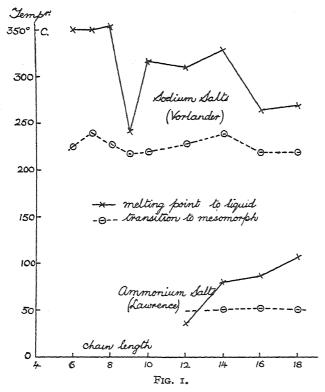
<sup>&</sup>lt;sup>2</sup> O. Lehmann, Ann. Physik, 55, 81, 1918.

<sup>&</sup>lt;sup>3</sup> Liepatoff, Koll. Z., 43, 396, 1927. <sup>4</sup> G. Friedel, Alexander's Colloid Chemistry, I, p. 102.

<sup>&</sup>lt;sup>5</sup> Ber., 43, 3120, 1910.

or direct into the molten fatty acid. The results are also given in Fig. 1 and show some of the irregularity of the earlier work of Vorländer on the sodium salts, so that some other explanation is required. The fatty acid esters of cholesterol show a similar effect.<sup>6</sup>

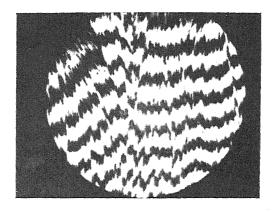
In the sealed tubes, the smectic mesoform invariably appeared in the centre of the tube while ammonium laurate, which passed directly from liquid to crystalline form, grew from the wall inwards. Microscopic examination of these four ammonium salts throws light on their behaviour. They can be heated without decomposition if care is taken as they are fairly stable in absence of moisture. Any decomposition is made evident at once in a preparation under a cover glass by evolution



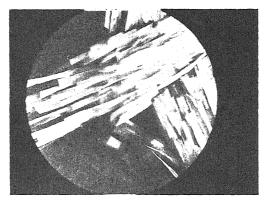
of bubbles of ammonia gas. Loss of ammonia leaving free fatty acid mixed with the salt also shows itself in a curious way; on cooling the liquid, rhythmic crystallisation occurs (Fig. 2 (a).

Fig. 2 (b)shows the laurate crystallising from the liquid and (c) the palmitate, thedarker part being the smectic form and the lighter fringent part the solid which is growing as pseudo-

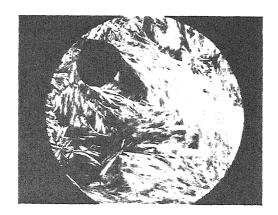
pseudomorph on the texture of the smectic mesoform. Observed this way, the interval between the appearance of the smectic and that of the solid seems much smaller than the bulk melting-points require. There is considerable supercooling of the smectic so that, when it does appear, its rate of growth cannot be controlled and the characteristic tangled structure results. No supercooling of the solid occurs. These facts can be explained by the assumption of a persistent surface layer such as has been described by Friedel for many substances. And, further, that this surface layer has the orientation of the solid form; so that it cannot seed the smectic but can always prevent supercooling of the solid. It also prevents the formation of the smectic form at the walls of the



(a)



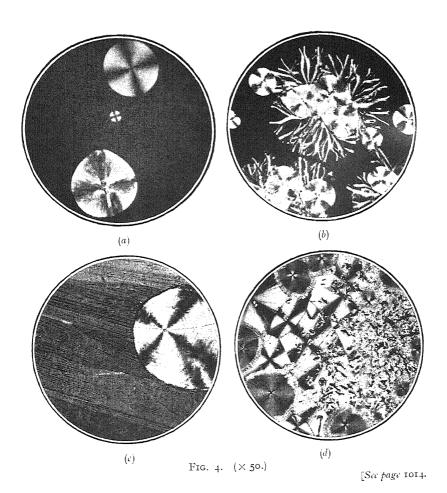
(b)



(c)  $(\times 50) \text{ (Crossed Nicols)}.$ 

Fig. 2.

[To face page 1010.



sealed tubes. The laurate, having no smectic form grows inwards from the wall, but if a specimen is heated well above its melting-point to destroy the surface layer, rapid cooling does then yield a smectic mesoform quite similar to its higher homologues. The behaviour of the ammonium salts seems quite similar to that of the cholesterol esters of these fatty acids.

A substance heated above its melting-point is usually described as isotropic, which rarely means more than that the liquid is not cloudy. The whole manner of appearance of the mesoform in the molten soaps suggests structure in the liquid. At the temperature of its appearance, which is quite sharp, the mesoform is seen suddenly throughout the liquid. The difference of refractive indices is quite small. It seems clear that the transition temperature, insofar as it is a constant,\* is not defined by the chain length, of which it is independent, but by the nature of the kation. The presence of a double bond makes no difference, as shown by ammonium elaidate, which has a similar transition temperature. The oleate, however, is exceptional in that no fully crystalline form exists at room temperature. It is dimorphous with the transition point curiously enough at 51°. It thus appears to be an exception to Friedel's rule that no substance exists in more than one smectic form.

#### Soap/Water Systems.

There is still confusion concerning the forms in which soap/water systems exist. This is due to nomenclature—particularly with respect to the application of the phase rule—and to the complex nature of the forms themselves. The time factor is also important, since equilibrium is in some cases reached only after long intervals. McBain 7 defines the possible phases as follows:

Lamellar crystals.

Curd soap.

"Neat" soap (containing about 30 per cent. of water). Smectic.

"Middle" soap (containing about 60 per cent. water). Also liquid crystalline.

Isotropic liquid.

Gels are not a separate phase. They can be prepared isotropic to light and to X-rays.

The phase rule has been applied to these systems, and shows clearly how narrow are the limits in which the mesoforms exist—a fact which explains some of the contradictory statements which have appeared concerning the existence or non-existence of these for some soap/water systems. It is not realised generally, however, that the phase rule is not applicable to colloidal systems without grave risk of error. Often it is impossible to state whether one phase is present or two. Optical heterogeneity is not a final proof of the presence of two phases. Uniform composition is not a fundamental distinction of a single phase, but merely a working one. It is finally incompatible with the conception of atoms and molecules. For most systems, however, the large number of such kinetic units travelling with high velocity in their medium produces the degree of homogeneity defined as uniform for the phase rule. In systems such as the soaps, there must come a point where the particles have

<sup>\*</sup> A cooling curve of ammonium palmitate showed no discontinuity other than that at the melting-point.

7 Alexander's Colloid Chemistry, I, p. 137.

reached a size such that the system is no longer uniform to physical tests but in which no new phase—as defined by the existence of an interface—has appeared. In a recent paper on the sodium oleate/sodium chloride/water system, it is shown that at 25° there is one more degree of freedom than is allowed by the phase rule.8 This is attributed to variation of the solubility of the curd fibres with their diameter. I have described elsewhere how, from a homogeneous isotropic solution of sodium stearolate, threads of soap fibres can be drawn out on the end of a glass rod.9 These are not the separate soap curd phase, but bundles of soap micelles which also are thread or ribbon-shaped. There is little exact knowledge of the degree of polydispersity of soap solution in real equilibrium nor even of the actual range of dimensions over which either soap micelles or soap curd fibres can exist. The fundamental distinction is that, in the micelle, the polar groups are holding it in solution. whereas the curd has separated as an insoluble phase, which suggests association by the polar groups in the same manner as in the lamellar crystals, so that the exterior of the curd is hydrophobic. The resulting interface, curd/soap solution, is not apparent since adsorption of molecularly dispersed soap occurs, the hydrocarbon chains being attached to the hydrophobic exterior of the curds. This explains the regularity with which large curds build themselves up, and it supplies a picture of the easy reversibility of soap curd and micelle which delays equilibrium. Adsorption of soap in this way upon a small curd fibre transforms it into a micelle. Given sufficient small curds peptised by adsorbed soap, any sudden lowering of solubility will bring about a continuous linking up of all these particles. Gelatinisation of a soap solution seems to be this process, the steep solubility/temperature curve helping to maintain homogeneity.

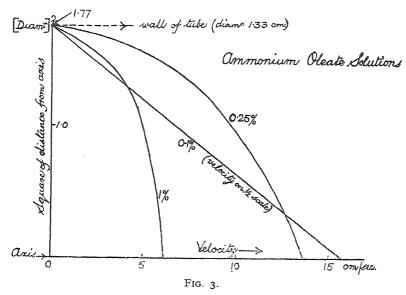
### Colloidal Mesoforms of Soap Solutions.

The liquid solution phase is usually described as "isotropic." seems to be to emphasise a difference between this phase and the crystalloidal anisotropic liquid phases rather than to indicate a result of experimental observation. In 1902 Krafft pointed out that quite dilute solutions of heptadecylamine oleate and erucate were strongly doubly refracting. In solutions of the common soaps, double refraction is not easily observed, but mechanical anisotropy is, in some cases, marked. The most striking example is ammonium oleate. 10 A I per cent. solution of this soap in water when rotated in a bottle does not slow down and come to rest like a normal liquid but recoils, often as much as 180°. Of course, the Poiseuille equation is not obeyed by such a solution, since it does not flow as a Newtonian liquid, with linear velocity a function of the square of the distance from the axis of the tube. In this laboratory, therefore, direct measurements have been made of the velocity distribution in flowing ammonium oleate solutions. (My method will be published shortly with a full description of the apparatus which is also a viscometer working on a new principle.) Fig. 3 shows the velocity distribution in some ammonium oleate solutions. The actual velocities are plotted against the square of the distance from the axis, zero velocity being at the radius of the tube squared. The object of plotting the results in this manner is that with Newtonian flow a straight line is obtained.

E. L. Smith, J. Physic Chem., 36, 2455, 1932.
 A. S. C. Lawrence, Koll. Z., 50, 12, 1930.
 Hatschek, Viscosity, p. 190.

Deviations are then obvious as in the I per cent. and 0.25 per cent. ammonium oleate solutions. For water and 0.1 per cent. ammonium oleate solution (at high rate of flow) straight lines were obtained; 2 per cent. ammonium oleate, when dissolved in 20 per cent. glycerin instead of water, also gave a straight line; 0.5 per cent. gelatin solution shows anomalous flow though to a smaller extent. Myosin is already known to show marked stream double refraction. We have found that the nature of its flow depends upon the amount of electrolyte present, and hence on the degree of its dispersion. A solution containing one concentration of electrolyte flows as a Newtonian liquid; with another concentration, the flow is quite anomalous.

These examples of anomalous flow show two main points. The centre of the tube, where the velocity is greatest, is also the region of maximum anomaly due to the structure of the solution; and, secondly, the liquid near to the wall of the tube travels much faster than the



parabolic relation requires. The structure in the liquid endows it with elasticity; but this structure, whatever its nature, must become progressively less as the wall of the tube is approached. Correspondingly, the resistance to flow decreases, and so causes the apparent slip near to the wall. Glass wool in a bottle provides an excellent analogy on a larger scale. It is amorphous as a whole, but it has structure such that it moves as a plug, slipping at the wall, since the internal structure does not include adhesion to it.

The cause of the elasticity of soap solutions would seem to be the thread-shaped micelles; these are made up of molecules lying side by side, so that their length is much greater than their width. In the flowing liquid such threads stretch—many beyond their elastic limit—but some do not pass it and are responsible for the elastic recoil of the solution. Its flow is a mixture of shearing and stretching.

<sup>&</sup>lt;sup>11</sup> Von Muralt and Edsall, Trans. Farad. Soc., 837, 1930.

## Structure in Crystalloidal Solutions.

The soaps discussed and also brom-phenanthrene-sulphonic acid pass through complex anisotropic liquid forms because of the nature of their molecules; both directly (i.e., crystalloidally) as a result of their form and constitution, which leads to the smectic form, and indirectly through colloidal association and its consequences. In this laboratory other substances have been found which are not colloidal, but which pass through a mesoform during crystallisation. Lithium tartrate is the best example so far observed. If a solution of the neutral salt is boiled down until crystals begin to appear, the solution may be cooled without any growth of these; nor is there any re-dissolution. If, now, the cold solution is left to stand and evaporate at room temperature for several days, a white microcrystalline powder is deposited. If the evaporation be carried out in a thin film on a glass slide, the mesoform is observed. If alcohol is added to the solution, a liquid separates and then crystallises.

That crystallisation occurs at a reasonable rate at 100° but not at room temperature suggests that, at the lower temperature, rate of growth of nuclei has become vanishingly small while the rate of formation of nuclei remains much the same; and that at 100°, the rate of growth is increased largely while the rate of formation is not (or even decreases). That this is not the explanation is proved conclusively by the fact that the cold and hot forms of the salt are not identical; as shown by X-ray examination kindly made for me by Mr. Bernal.

The appearance of the mesoform is influenced by several variable factors; temperature, supersaturation of the solution, humidity of the atmosphere in which the evaporation is taking place. However, a good idea of the series of changes is given by Fig. 4 (a), (b), and (c). (a) shows two liquid crystalline drops which are first formed in considerable numbers. This photograph also shows the next stage in which crystallisation is occurring from the mesoform. (b) shows the beginning of normal crystallisation in the liquid but very viscous solution still remaining, and (c) is the final stage where the crystallisation is complete. This final stage is rarely reached so definitely owing to the enormous viscosity of the solution. If, however, the preparation is warmed when in stage (b), small coloured plates of the crystalline form appear in large numbers until all the water has evaporated.

Lithium succinate does not exist in a mesoform, but its solutions show a peculiarity which throws light on the behaviour of lithium tartrate.

If a solution of such concentration that it contains a few crystals is boiled violently for a few minutes, crystals suddenly appear in a shower; 100 c.c. deposited 5.6 gm. while the mother liquors contained 31 gm. It seems, therefore, that the 5.6 gm. is in solution as a highly hydrated complex. This is probably the same type as the liquid precipitated

from the tartrate solution by alcohol. The very soluble lithium malate is similar to the succinate; but the much less soluble acid lithium tartrate shows no peculiarities.

There is an interesting resemblance between lithium tartrate solutions

and molten pentaerythritol-tetrapalmitate.\*

On cooling, this substance forms a mass of liquid crystal spherulites which are black and white and, among them, a few of higher birefringence and distinct radial structure (Fig. 3 (d)). These latter are usually yellow. On warming, the liquid crystalline part shows traces of radial structure and at 72° changes sharply to a mass of needles which melt at 84°. These form the confused structure on the right-hand side of the photograph. The temperature has been taken a little higher on this side, the left side not having reached 72°. During this time, the yellow patches have not changed but, beginning at 68°, crystallisation starts from around them in the liquid crystalline part, the rate increasing as the temperature rises. Above 84°, therefore, the original yellow patches remain surrounded by a mass of small crystalline plates. At 90.5° both of these melt together, and are therefore identical. The substance presents other peculiarities which have not yet been investigated.

The cases discussed here suggest need for further examination of solutions. The interest of the observations described is not in the light that they throw upon liquid crystals generally but rather in that the formation of liquid crystals from solution points to structure in the liquid from which they appear. Structure in solutions is less simple than in anistropic melts, and the optical methods which have been so successful with the latter must be less so in solutions. Any solution having a structure may be expected to have a high "viscosity". If this property is used for investigating them and measurements taken by one of the usual flow type viscometers, the results will be useless. Not because they are necessarily incorrect but because, unless precautions are taken, it is not known whether true viscosities are being measured at all—which are correct and which are not. The extent of the anomaly varies with rate of flow, temperature, concentration of the solute and, in many cases, with the history of the solution.

Theoretical work is being done on the effect of particle shape on viscosity, 12 but it is equally, or even more important, that size should be considered. Systems in which orientation of a peculiarly shaped particle is the determining factor are not of the type commonly occurring. These are solutions in which anomaly and structure result from the interrelation of the particles—particles which are still in solution but whose freedom as kinetic units is restricted. The problem is the cause of this restriction and its variation with external conditions.

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<sup>\*</sup> Kindly supplied to me by Mr. N. K. Adam. <sup>12</sup> W. Kuhn, *Z. physik. Chem.*, **161**, 1 and 427, 1932.

## INVESTIGATIONS AND CONSIDERATIONS CON-CERNING PARACRYSTALLINITY.<sup>1</sup>

By Friedrich Rinne (Freiburg i. Br.).\*

Received in German on 6th January, 1933, and translated by D. Shoenberg.

A very valuable scientific plan was accomplished in the Zeitschrift für Kristallographie, vol. 79 (Series I-4), pp. I-347 (1931). This was concerned with the combined efforts of a number of workers on the much debated subject of "liquid crystals." Although no unanimity was achieved by the exchange of opinions, the publication was successful in that the many experiments were once more discussed by a large circle of those interested, and a stimulus was given to further investigation.

It is a pleasure to me, on the basis of some of my own investigations and speculations, to take part in the renewed discussion inaugurated by the Faraday Society, and in what seems especially important to me: the experimental demonstrations and oral conferences in London. From the point of view of my own work, there are four sections which I should like to contribute to the discussion:—

- I. Methods of formation.
- II. Miscibility.
- III. Inclusion of natural organic objects in the paracrystalline group.
- IV. Notes on Nomenclature.

#### I. Methods of Formation of Paracrystalline Materials.

#### 1. The Thermal Method.

The classical experimental illustration of paracrystalline substances follows generally the scheme:—

(I) crystalline  $\rightleftharpoons$  (2) paracrystalline  $\rightleftharpoons$  (3) isotropic melt.

It is, however, self evident, that it is not practicable, as is sometimes alleged, to conclude that the above scheme is of an all-embracing character. In fact, it is not always so. Apart from the fact that often monotropy occurs instead of enantiotropy, a large number of paracrystalline materials do not transform into an isotropic melt when the temperature is raised. Others do not attain the crystalline state on cooling. Just as with proper crystals, the grouping of the particles in paracrystals does not depend upon the method of formation or disappearance. For this, only such properties are suitable which hold for the group as a whole. In this sense garnet is called a crystal although this mineral decomposes before its melting-point and is not reformed

<sup>&</sup>lt;sup>1</sup> At suitable points in the following, the author will explain what facts lead him to prefer the word " Paracrystals" to other names.

<sup>\*</sup>The Faraday Society profoundly regrets that Geheimrat Professor Dr. Friedrich Rinne, who was looking forward to being with his colleagues in London at this meeting, died in Freiburg on 12th March after a short illness. Professor Rinne had corrected the proof of the translation of his valuable contribution to the meeting a short time before his death.

from its melt. Similarly it would be quite justifiable to include in the paracrystalline group even a substance, which did not show both end states of the scheme :-

(1) crystalline  $\rightleftharpoons$  (2) paracrystalline  $\rightleftharpoons$  (3) isotropic melt,

provided it showed the properties of the second state of the series. D. Vorländer 2 quite rightly includes in the class of "liquid crystals" crystalline liquid substances which form no isotropic melts, but on the contrary decompose earlier on heating; in fact he points out that substances with this behaviour exhibit the crystalline liquid characteristics remarkably beautifully.

It is necessary to point out these facts, since they are of special importance in arriving at an understanding of the existence of the finestructure types in question. For example, D. Vorländer states that

$$\mathsf{CH_3} \!\!-\!\! \mathsf{CO} \!\!-\!\! \mathsf{O} \!\!-\!\! \mathsf{C_6} \mathsf{H_4} \!\!-\!\! \mathsf{CO} \!\!-\!\! \mathsf{O} \!\!-\!\! \mathsf{C_6} \mathsf{H_4} \!\!-\!\! \mathsf{CO} \!\!-\!\! \mathsf{O} \!\!-\!\! \mathsf{C_6} \mathsf{H_4} \!\!-\!\! \mathsf{COOC}_2 \mathsf{H_6}$$

is an enantiomorphic liquid crystal with an existence range from 142° to 282°, i.e. of 140°; with the ester containing 4, instead of 3 C6H4. groups, the region of paracrystalline stability is increased from 187° up to red heat, at which the substance decomposes. Thus its paracrystalline modification is maintained over a temperature interval of approximately 300° C.—a sign of particularly strongly marked paracrystallinity. Further it should be observed that many liquid crystals evaporate or distil before they transform into an isotropic melt. According to Vorländer, in the case of dianisal benzidine the crystalline liquid disappears at ordinary pressures and the isotropic melt cannot be reached. It is naturally not possible to omit all such substances.

Finally it can be shown that typical materials in the paracrystalline class can be obtained, quite independently of thermal mechanism, i.e., without any heating. This especially instructive case is dealt with in the following two sections.

## 2. The Transformation of a Crystalline Substance into a Paracrystalline Modification at Low Temperatures under the Influence of Water.

As a very clear example of the transformation of a crystalline into paracrystalline fine-structure types without heating, I chose Landquist's bromo-phenanthrene sulphonic acid 3 for closer study. On mixing the crystal powder with water a paste is obtained, which after vigorous squeezing with the "coverslip" provides a very suitable preparation for microscopic examination. It shows the transformation from the crystalline to the paracrystalline modification remarkably clearly and beautifully when studied optically with polarised light. These phenomena are quite comparable with the best classical examples of paracrystals obtained by heating.

A convenience of this procedure is that it allows of observation at ordinary temperatures.

In preparations of hydrated bromo-phenanthrene sulphonic acid we observe in general an  $\alpha$ -paracrystalline (nematic) and a  $\beta$ -paracrystalline (smectic) formation, varying according to position; the former occurs when the paste meets the surrounding water and the latter in the interior of the specimen. When water is present in quantity, pre-

D. Vorländer, Chem. Krist. d. Flüssigheiten, p. 34.
 H. Landquist, Koll. Z., 19, 113, 1916; F. Rinne, Z. Krist., 82, 379, 1932.

parations are obtained in which the  $\alpha$ -modification is predominant (Plate I, Fig. I). At the edges it readily resolves itself into a network of drops and single drops whose  $\gamma$  spherulitic structure appears very prettily in the radial direction. With larger compact masses the material looks like "watered silk" or Damascus steel (Fig. I, Plate I), and has undulate extinctions corresponding to distorted spherulites. On drying, the  $\beta$ -paracrystalline phase appears more and more, swallowing up the nematic modification. The limit between the two is always sharp as G. and E. Friedel 4 have already emphasised. This  $\beta$ -paracrystalline hydrated bromophenanthrene sulphonic acid is more viscous than the  $\alpha$ -paracrystalline modification and is of needle-like cross-striped texture (Plate I, Fig. 2). When the coverslip is pushed backwards and forwards the material arranges itself in stripes and these appear longitudinally as  $\alpha$ , and transversally as  $\gamma$ .

When studied with X-rays the material in question also shows up its paracrystalline nature. The Debye-Scherrer photograph of the  $\beta$ -paracrystalline modification (copper radiation:  $\lambda = 1.539$ , 40 kv. and 25 ma., 8 hours' exposure) shows, in contrast to the wealth of lines obtained with the crystalline substance, a sharp ring corresponding to 3.47 Å, which corresponds to a 3.40 Å ring of the crystalline phase. The fine-structure periodicity difference of about 0.1 Å is to be interpreted as a distinguishing d-value of the crystal on transformation

into the paracrystal.

The swelling shows that the transformation causes an increase of a structural periodicity of the fine structure. When water is abundantly present a broad blurred zone replaces the sharp ring. Finally, a solution is obtained. Complete evaporation leads back to the crystalline modification. Heating of the crystal powder leads to de-

composition and paracrystalline types are not formed.

As an explanation of the fine-structural breaking up of the three-dimensional periodic crystal structure into the singly and doubly periodic paracrystalline type, under the influence of water, the high dielectric constant 81 of the latter may be adduced. This means a powerful diminution of the electrochemical fields into which the water penetrates. In this sense the course of the process corresponds to a heating, which at the same time loosens the fine-structure combination. Now just as the warming of crystalline substances often produces abrupt and repeated changes from one regular structure to another and finally a general confusion of fine structure, so, similarly, the absorption of water by bromophenanthrene sulphonic acid produces first the  $\beta$ -paracrystalline, then with increased action of the water, the  $\alpha$ -paracrystalline modification, and finally an isotropic solution.

That loss and reabsorption of water alter structure is also known, for example, in the case of *zeolites.*<sup>5</sup> In the latter case, also, absorption of water can be associated with a structural change. The case of Skolezite <sup>6</sup> should be especially noted in this connection.

## 3. The Formation of Paracrystals from Cold Solutions.

F. M. Jäger has already shown that on addition of acetone to a cold saturated solution in acetic ester of phytosterin valerate the latter

<sup>&</sup>lt;sup>4</sup> G. and E. Friedel, Z. Krist., 79, 13, 1931.

<sup>&</sup>lt;sup>5</sup> F. Rinne, Berichte d. pr. Akad. d. Wissensch. Math. Phys. Klasse, 46, 1163, 1890; Fortschr. d. Mineral, 3, 159, 1913.

<sup>6</sup> F. Rinne, Jahrb. Mineral, II., 51, 1894.



Fig. 1.—Wetted  $\alpha\text{-paracrystalline}$  (nematic) bromophenanthrene sulphonic acid. Enlarged 1:150 + Nicols.



Fig. 2.—Wetted  $\beta\text{-paracrystalline}$  (smectic) bromophenanthrene sulphonic acid. Enlarged  $\mathfrak x:\mathfrak x_{75}$  + Nicols.

[To face page 1018.

## PLATE I. (cont.).

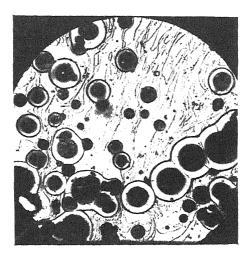


Fig. 3. Anisal  $\alpha\text{-benzolazo-}\alpha_T\text{-naphthylamine}$ . Spherulitic crystals and paracrystalline resin-like hard-core (Grundmasse). Enlarged 1:110 ordinary light.

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definitely separates out as a paracrystal. The author studied this kind of formation of para-crystals from cold solutions of anisal- $\alpha$ -benzolazo- $\alpha_1$ -naphthylamine. The results obtained in this case illustrate especially well the memorable statement of R. Bunsen in 1861, that melts and solutions are equivalent when regarded from a physical point of view.

Thus if crystals of anisal-\alpha-benzolazo-\alpha\_1-naphthylamine or paracrystalline formations obtained from the melt are touched with cold acetone or ether, the paracrystalline phase separates out of the rapidly evaporating solution in spite of the low temperature. It appears in the form of innumerable very small round or longitudinally crooked patterns. That this product of a cold solution is indeed the same paracrystalline phase as that obtained from the isotropic melt at 110° C. is shown by its unmistakable optical properties, especially on application of the extinction test. Instead of the former fine granular aggregate between crossed nicols, a unique extinction is obtained. The extinction occurs parallel and perpendicular to the length. Correspondingly a uniform pleochroism occurs: deeper colours (approximately brownish-yellow) for the oscillations parallel to the rods and bright yellow transversely. At the thinnest places of the paracrystalline modification a typical deep moss green stands out very markedly. All these phenomena are met with also in the formation of paracrystals from a melt.

This example of anisal- $\alpha$ -benzolazo- $\alpha_1$ -naphthylamine has also the great advantage that a paracrystalline modification can be obtained from the isotropic melt of the substance as well as from its cold solution. Thus we are provided with the desired opportunity of comparing the state in which the substance occurs by means of the latter type of formation with the state obtained by separation from the melt. The two are identical.

## 4. The Coherence of Paracrystals, especially the Super-cooling of Paracrystalline Substances to a Solid.

The physical, as well as the chemical, nature of every material is based on its fine structure. On this also depends the internal coherence of the substance. From this point of view clear examples of systems of extremely low coherence are provided by gas, and, as those of weak consistency, by normal liquids which also exhibit examples of more considerable viscosity. Thus, clearly, the coherence varies considerably within the bounds of one and the same fine-structure type. Materials classified as crystals and paracrystals link on. The approximately three times closer fine structure of crystals implies in general a considerable strength. It is, however, well-known that within these limits many extremes of coherence take place from the strength of diamond to the feeble inner coherence of crystalline amalgam, or of potassium or even lower. Thus it is quite unsuitable to take a certain standard of coherence as, for example, that of diamond, as a universal criterion of the crystalline state. Exactly the same circumstances obtain for paracrystalline materials, in the opinion of G. and E. Friedel, 9 as well as of the author. Within the classification of fine structure many gradations of coherence are possible and known. In general the α-paracrystalline (nematic) structure is associated with greater internal motion

<sup>&</sup>lt;sup>7</sup> For literature see Wo. Ostwald, Z. Krist., 79, 222, 1931.

<sup>&</sup>lt;sup>8</sup> R. Bunsen, Z. deutsch. geol. Ges., 13, 61, 1861. <sup>9</sup> Cf. G. and E. Friedel, Z. Krist., 79, 1, 325, 1931.

Generally a greater viscosity occurs in  $\beta$ -paracrystalline (smectic) materials; this is associated with the more complex fine structure (compared with the  $\alpha$ -paracrystalline texture). So far as is known, it does not show the Brownian motion, unlike the  $\alpha$ -paracrystalline modification. From all this it is clear that a given degree of coherence, for example fluidity at ordinary temperatures, is no general criterion of the paracrystalline group. As extremes of the group we find, on the one hand, internal mobilities greater than that of water, while, on the other hand, paracrystals can be so hard that the name liquid in the sense of mechanics is quite inapplicable. The author has investigated such a case with the above mentioned anisal- $\alpha$ -benzolazo- $\alpha_1$ -naphthylamine.

This substance, which is most interesting from many points of view, melts at 150°. It was first studied by D. Vorländer and his pupils G. Kreiss and Ch. Kuhrmann. The wine-red liquid in thin layers transforms on cooling at 110° C. into the paracrystalline state. From the now yellowish-red base of the substance obtained, or already from the isotropic melt, large yellowish-green  $\alpha$ -spherulites of the monoclinic system are formed, which show a magnificent pleochroism, which will not be further described here. When the temperature is lowered below 75°, numerous small yellow (in case of thin preparations) or darker spherulites are formed in addition. These exhibit a strong pleochroism in the dark red as well as alternating black and yellow. If the cooling is not too slow there remains a paracrystalline residue, which, moreover, is the unique type of formation easily obtained by rapid cooling of the isotropic melt or of the newly-formed paracrystalline modification (Plate 1, Fig. 3).

With lowering of temperature the viscosity of the paracrystalline material increases and finally (at 10°-15°) rises strongly to hardness. D. Vorländer, through his pupil, A. H. Krummacher, has published

the quantitative values for this.

In the microphotograph the liquid nature of the paracrystalline material is very clearly recognised at higher temperatures by its streaming phenomena. This soon ceases on cooling, and even pressure with a needle no longer produces any flowing.

The substance has become hard and can certainly no longer be described as a liquid formation. Its paracrystalline nature, however, resembles in every respect that at higher temperatures. Analogous

examples are to be found in large numbers.

## 5. The Miscibility of Paracrystalline Substances.

D. Vorländer has established that a fundamental stereochemical feature of "liquid crystals" consists of an elongated molecular form, even though this fine-structure type is not an absolute condition. Alkali salts of carboxy acids, such as sodium benzoate (which does not exhibit any favourable parasubstitution of the elongated form) and sodium m-bromobenzoate, are all liquid crystals in spite of small molecular elongation and in spite of m-substitution, and therefore ex-

12 Full exposition by D. Vorländer in Chemische Kristallographie der Flüssigheiten, 1924. More recent survey: D. Vorländer, Physik. Z., 31, 428, 1930.

<sup>D. Vorländer brings this out very drastically, Z. Krist., 79, 346, 1931.
D. Vorländer, Z. angew. Chem., 43, 13, 1930; G. Kreiss, Dissertation, Halle, 1925; Ch. Kuhrmann, Dissertation, Halle, 1926.</sup> 

amples of the fact that molecular-energetic conditions also play a part in this case.

Now just as, by way of comparison, atomic dimensions, that is to

say, spacial relations, play a very considerable rôle in regard to fine-structure arrangement in crystals, so it appears from the investigations of R. Schenck 13 and D. Vorländer that molecular 170° isomorphology in crystalline substances associated with considerable miscibility. Such structure combinations occur not only with similar sub- 150° stances such as paraazoxyanisol and para-azoxyphenetol, but also with compounds which are chemically very different, e.g., para-azoxyanisol with methoxycinnamic acid (Text, Fig. 1). The chemical differences are more or less smoothed out by the similarity of molecular type.

From the point of view of miscibility, the lipoids, cerebrosides and phosphatides present extremes and therefore contain most significant possibilities. Cerebron, cerasin, nervon, as well

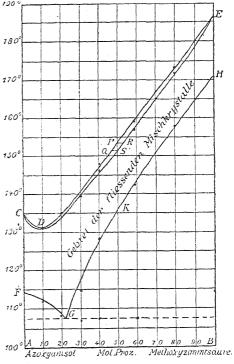


Fig. 1.—Miscibility of paracrystals (R. Schenck).

as lecithin, kephalin and sphingomyelin, are indeed all substance groups of a very complex kind. As an example, the formula for cerebron  $C_{48}H_{38}NO_9$  is quoted:—

In the case of myelin formation, a further, but on the other hand, purely chemical complication is the strongly changing water content. Physically the cerebrosides and phosphatides permit of classification in a simple scheme.

Having regard to these significant relations the author studied a

13 R. Schenck, Kristallinische Flüssigkeiten und flüssige Kristalle (1905).

series of these substances both microscopically and with X-rays. For making the X-ray diagrams I am indebted to Drs. Ganter and G. Böhm, as well as to my colleague, Herr Klenk, in Tübingen, for kindly providing the materials.

On warming the whitish granular material the cerebrosides and phosphatides become softer and softer. At the same time their double refraction appears more distinctly, until the completely clear isotropic melt sets in (transformation temperatures: cerebron 212°-215°; cerasin, 180°-187°; nervon, 180°; sphingomyelin, 196°-198°. In the case of lecithin no exact data are yet available.) On cooling under a coverslip a flaky tufted mass with grey polarisation colours is formed, or spherolithic patterns with optically negative radii are formed more or less clearly—in the case of sphingomyelin in a very marked manner (Plate 2, Fig. 1).

Moistening with water or with glycerine containing water, leads, especially on heating the preparations, to an interesting morphological multiplicity of soft spherulites and myelin forms.

Especially susceptible for this, as is well known, is lecithin, which has an incipient yellow colour due to decomposition, since this substance as a pure white material does not give the myelin reaction. Above all, small spherulitic spheres are formed with optically positive radii (Plate 2, Fig. 2). From them there grow out excrescences probably due to a local diminution of surface tension. These lead further to very peculiar, long, sluggishly moving masses, often with remarkable configurations of turns, twisted and narrow spiral wrappings and also with swellings at the head (Plate 2, Fig. 3/4). The double refraction in this case falls to a very small value as the water content is increased. In all these formations we are dealing with axially distorted spherulites with optically positive radii.

A Debye-Scherrer diagram taken by Dr. G. Böhm (copper radiation 45 kv. and 25 ma.; exposure 8 minutes with a Mark tube) of melted and resolidified, clearly spherulitic sphingomyelins and also of cerasin, gave only a single sharp ring corresponding to approximately 4.8 Å (Plate 3, Fig. 3). These photographs agree, therefore, with the photograph of a  $\beta$ -paracrystalline state. The same was obtained from a mixture of 3.5 gms. lecithin with 4.5 gms. water. On the other hand, photographs with cerebron under the same conditions gave, besides the sharp ring at 4.8 Å, sharp inner interference lines, which point to crystalline conditions. This is explained by chemical decomposition of the easily transformable substance. This conclusion is all the more justified, since with lecithin which has become brownish red microscopic investigation shows a wealth of very delicate little needles. Pure lecithin gave only the fairly sharp above-mentioned interference ring, which signifies a  $\beta$ -paracrystalline structure.

Incidentally, it is relevant in this connection, that with cerebron, genuine crystals are also formed, <sup>15</sup> which go over into a paracrystalline modification and then into an isotropic melt, on heating.

These substances follow the well-known thermal scheme

crystalline ≥ paracrystalline ≥ isotropic melt.

H. Zocher and V. Birstein, Z. physik. Chem., 142 A, 177, 1929.
 H. Thierfelder and E. Klenk, Der Chemie der Cerebroside und Phosphatide (1930).

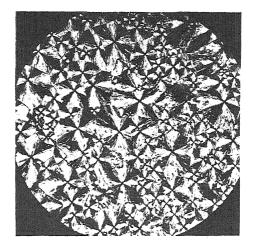


Fig. 1.—Spherulitic  $\beta$ -paracrystalline (smectic) Sphingomyelin  $\times$  Nicols.

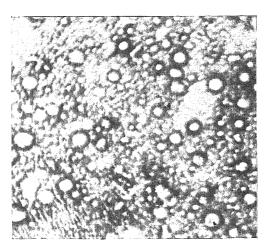


Fig. 2.—Spherulitic paracrystalline wetted lecithin. Ordinary light.

[To face page 1022.

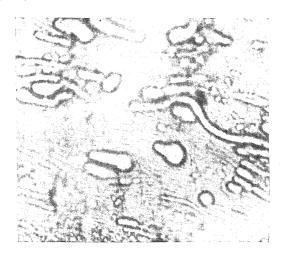


Fig. 3.—Sloughish paracrystalline wetted lecithin. Ordinary light.

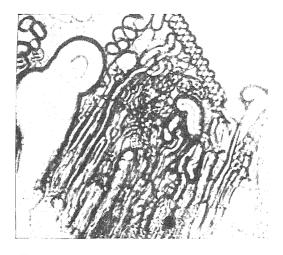


Fig. 4.—Myeline paracrystalline wetted lecithin. Ordinary light. [See fage 1022.

## 6. Collective Paracrystallisation and Inoculation of Paracrystalline Substances.

Corresponding to collective crystallisation as a combination of crystalline parts of an aggregate (e.g., of gold or iron or calcite and many other materials) into larger crystals, or as with aluminium to a single pattern of this kind, there exists collective paracrystallisation. It takes place often with astonishing rapidity and completeness, e.g., with cholesterin chloride. At the same time the optical axes provide indications of the principal structural directions over large stretches of the microscopic pictures perpendicular to the object carrier. In consequence one observes in the conoscope an interference pattern like that of a uniaxial, and in this case, negative, crystal. In this connection special reference should be made to the excellent pictures made by W. Berger in the atlas of D. Vorländer and H. Hauswaldt: Achsenbilder flüssiger Kristalle (1909). Also to the admirably exact photographs taken by W. Berger in natural colours.

Such combinations of directed paracrystals are, from the point of view of fine structure, often so strong that, at least at rest, they may be preserved for some hours on cooling to room temperature. A pretty and perhaps hitherto unknown experiment in this connection may be performed with a mixture of anisal- $\alpha$ -benzolazo- $\alpha_1$ -naphthylamine and cholesterin chloride. The supra-cooling of the established paracrystalline mixture modification lasts some hours and the separation of crystalline spherulitic cleavages is very markedly suppressed. It is this behaviour which opposes so exceptionally the rapid crystallisation of the pure first-named substance.

The marked stability of substances combined by collective paracrystallisation is connected with the fact that even in the case of chemically different substances they act as norms of structural union. According to D. Vorländer <sup>16</sup> a small admixture of a substance with a very large natural tendency to set uniaxially (e.g., p-ethoxybenzalaminoα-methylcinnamic acid) is sufficient to bring randomly arranged liquid paracrystals into a uniaxial arrangement. From this point of view it is also worthy of mention that, according to D. Vorländer, minute quantities of circularly polarising admixtures can transform optically inactive crystal liquids into strongly active and pleochroic ones. Finally, it is significant that many substances, not liquid crystalline in themselves, become so on melting together with others which are liquid crystalline. Their ability to paracrystallise must therefore have been increased.

## 7. Note on Paracrystalline Colloids and Aggregates.

As is well known the only basic feature of colloids is that the size of the parts should lie between molecular and microscopic dimensions. Thus in deciding whether a substance belongs to the colloid class, it is completely irrelevant whether it has a random or a regular fine structure. Similarly, we do not have to consider whether it is mixed with materials of greater or lesser colloidal dimensions, or with other colloids.

Thus, fundamentally, the door to the region of colloids is open also to paracrystalline materials. <sup>17</sup> It would be a fatal mistake, retarding both

D. Vorländer, Chem. Kristallogr. d. Flüssigkeiten, p. 57.
 See Wo. Ostwald, Z. Krist., 79, 222, 1931.

scientific and technical progress, if colloid dimensions and paracrystallinity were declared incompatible.

This would be as unjustified as the exclusion of colloid particles of quartz or gold from the crystal class. Both granitic pegmatite quartz and the quartz of colloid dimensions initially developing in kieselgel are crystalline. Similarly, macroscopic gold and the colloidal gold particles in gold glass are genuine crystals. In the latter connection there are, as is well known, the beautiful X-ray proofs of P. Scherrer.

It is important to emphasise the above, since such conditions have an especially great importance in the organic domain. 18 The colloid paracrystalline plays a very significant rôle there. In the conviction that the study of the fine-structure classification should not exclude the organic, the following considerations are devoted to organic paracrystals.

## 8. Organic Paracrystals (Bioparacrystals).

In view of the astonishingly great multiplicity of organic nature it would be a biologically most surprising fact if in the structures of the millions of varieties in the plant and animal world all three types of fine structure of matter (random fine structure (atactic), paracrystalline and crystalline forms) did not occur. Actually all three are represented in the materials of organisms, with the paracrystalline fine structure often quite predominant, however. Like crystalline material it satisfies most satisfactorily many very important biological requirements. This is the case with the fibrous and string-like formation so often met with organically, as well as with braided textures. In all these, the physiologically necessary softness, suppleness and pliancy (with the preservation of the general type of formation), and at the same time the great strength in the direction of the fibre, are favoured by the combination of paracrystalline (and very often crystalline) molecular "threads" and micelles. A gel-like fine-structural "bundle texture" is of exceptional utility for the physiological processes of orientated contraction and re-expansion, as well as for the reciprocity between directed swelling and the fine-structural contraction.

In the above connection it is not without significance that many paracrystalline materials, without being bound together biologically, adopt forms reminiscent of such organic types. To this class, for instance, belong the nuclear spherulites and tube-like myelin forms of phosphatides. 19 M. H. Fischer and M. O. Hooper 20 have pointed out similar cases.

A further unusually important biological tendency of paracrystalline materials is the fine-structural mixture of many chemical substances in the colloid-submicroscopic micellar patterns. It is precisely on this account that a most important feature of many organic substances is obtained, viz., their chemical complexity and high chemical lability.<sup>21</sup> A large number of "biomolecules" or genes find their location within

<sup>18</sup> For the relations between organic and inorganic see F. Rinne, Grenztragen des Lebens, eine Umschau im Zwischengebiete der biologischen und anorganischen Naturwissenschaft, Leipzig, 1931.

F. Rinne, Koll. Z., 60, 288, 1932.
 M. H. Fischer and M. O. Hooker, Koll. Z., 11, 220, 1916.
 Cf. F. Rinne, Koll. Z., 61, 304, 1932.

paracrystalline materials, and not least important, water also, somewhat as in the case of zeolites <sup>22</sup> or albumen crystals.<sup>23</sup>

The apparent thermal obstacle, by which paracrystals should always form on heating crystalline materials, does not arise here, as is suggested above. On the contrary, paracrystals are able to form and persist even at the lower temperatures characteristic of the organic world.

## 9. Examples of Bioparacrystals.

## (a) Lipoid Drops.

These patterns are mentioned in an unusually abundant literature. We may mention here C. Mettenheimer (1857) as the discoverer of their double refraction, O. Herrmann who pointed out the relation with "liquid crystals," L. Aschoff and his students—especially R. Kawamura among the latter—and also S. Chalatow as successful physiological researchers.

An excellent survey of the facts is given by W. J. Schmidt in his work Die Bausteine des Tierkörpers in polarisiertem Licht.

In the case of lipoid drops we are concerned with the cholesterin ester of fatty acids or with mixtures of these and triglycerides. They are found, for instance, in many organs of human and animal bodies (which have become pathological), e.g. in large quantities in the fatty parts around the kidneys and also in degenerated blood-vessel walls. Significantly their thermal behaviour is analogous to that of many artificially prepared paracrystalline materials, i.e.

crystalline ≥ paracrystalline ≥ isotropic melt.

In the case of vertebrate animals the body heat causes lipoid drops to appear in the liquid paracrystalline state. Examination between crossed nicols proves them to be optically positive spherulites with double refraction of variable intensity. The latter is no doubt connected with the variety of substances in the mixture.

After all, there is no cogent reason for excluding these lipoid drops from the group of liquid paracrystals, which, indeed, no observer of the facts has done.

Possibly the so-called "blood dust" which is found for some hours in human blood after an abundant meal of butter, also belongs to the group. On account of the extraordinarily small dimensions of the particles (which show a Brownian movement) their paracrystalline nature has not as yet been investigated. It should be noticed that the dimensions of the above-mentioned certainly paracrystalline lipoid drops are sometimes also extraordinarily small. They appear, then, like an anisotropic cloud.

#### (b) Sperms.

Chemical Facts.—In sperm material we have a combination of nucleoproteins with other albumin substances. According to E. Fischer, Abderhalden, Thannhauser, Dorfmüller, Levene and London, as well as other workers, there are sound reasons for assuming the presence of elongated molecules in the mixture of the substances concerned. With

F. Rinne, Fortschr. d. Mineral., 3, 159, 1913.
 A. F. W. Schimper, Z. Krist., 5, 131, 1881.

regard to thymonucleic acid, Levene and London have established the following expanded zig-zag formula:—

$$\begin{array}{c} C_{39}H_{51}N_{15}P_{4}O_{25} = \\ HO \\ O = P - O - C_{5}H_{7}O \cdot C_{5}H_{4}N_{5} \\ HO \end{array}$$

$$\begin{array}{c} O = P - O - C_{5}H_{7}O \cdot C_{5}H_{5}N_{2}O_{2} \\ HO \end{array}$$

$$\begin{array}{c} O = P - O - C_{5}H_{7}O \cdot C_{4}H_{5}N_{2}O_{2} \\ O = P - O - C_{5}H_{7}O \cdot C_{4}H_{4}N_{8}O \\ HO \end{array}$$

$$\begin{array}{c} O = P - O - C_{5}H_{7}O \cdot C_{4}H_{4}N_{8}O \\ HO \end{array}$$

Morphology and Optics.—We select for brief discussion the sperms of Sepia officinalis, as being the most carefully studied examples, the exact knowledge of which is due to W. J. Schmidt.<sup>24</sup> They belong to the nematosperms, which consist of an extended chromatin head and a soft appendage made up of other albumen types (Text, Fig. 2). When the sperms penetrate into the egg the appendices are removed. The regularity of the development of these patterns is surprisingly great.



Fig. 2.—Sperm of Sepia officinalis (W. J. Schmidt).

In this connection W. J. Schmidt writes: "Every morphologist will be astonished to see the precision work of spermogenesis, which produces millions of sperms of a species

exactly agreeing in size and shape. This exact equality, reminiscent of mass production of delicate mechanisms, is characterised by the agreement of (optical) path difference; the latter, with the same material and constant direction of the beam, being a delicate test of equal thickness." For any unbiassed observer of this complete optical equivalence in the microscope, it is quite impossible to believe that a secondary double refraction, produced by pressure or tension, is in question.

In the case of chromatin we are concerned more particularly with a mass of material of a special nature, *i.e.* autonomously based optical anisotropy, and indeed, as with a part of the artificial paracrystals, with an optically negative uni-axiality. The axis of isotropy coincides with the longitudinal direction of the sperm heads. W. J. Schmidt found, by means of the imbedding method,  $\omega = 1.54$ ,  $\epsilon = 1.50$ , and therefore  $\omega - \epsilon = 0.04$  (or by application of the Berek Compensator, 0.05). This is approximately five times the double refraction of quartz (0.009) or equal to the strong optical anisotropy of biotite (0.041). Such high figures are also found with artificial paracrystals. For instance, E. Dorn and W. Lohmann obtained for optically positive ethoxy-benzalamino- $\alpha$ -methylcinnamic ethyl ester the figures  $\omega = 1.520$ ,  $\epsilon = 1.914$ , whence

<sup>&</sup>lt;sup>24</sup> W. J. Schmidt, Zool. Jahrb., 45, 177, 1928. See W. J. Schmidt, Naturw., 16, 900, 1928; and also F. Rinne, Naturw., 18, 837, 1930; Koll. Z., 56, 71, 1931; Zentralbl. f. Mineral. A., 233, 1931.

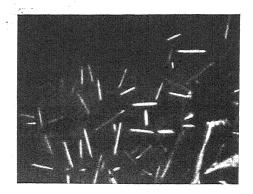


Fig. r.—Paracrystalline (D. Vorländer) para-azoxybenzoeacidethylester.  $\times$  Nicols.

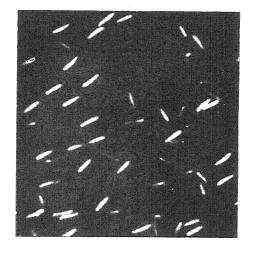


Fig. 2.—Paracrystalline sperms of Sepia officinalis.  $\times$  Nicols (W. J. Schmidt).



Fig. 3.—X-ray picture (Debye-Scherrer diagram) of  $\beta$ -paracrystalline (smectic) sphingomyelin. (See page 1022.)

PLATE III. (cont.).



Fig. 4.—X-ray picture (Debye-Scherrer diagram) of a dried muscle of Rana esculenta (G. Boehm and K. F. Schotzky).



Fig. 5.—X-ray picture (Debye-Scherrer diagram) of a living relaxed muscle of Rana esculenta (G. Boehm and K. F. Schotzky).

 $\{See\ page\ roz8.$ 

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 $\epsilon-\omega=0.394$  for sodium light.<sup>25</sup> The appendix for locomotive purposes has an optically positive nature in the direction of its length.<sup>26</sup> Probably an albumen component is predominant in it, whose bundle of fibrillar molecules is optically positive, as in the ovoglobulins. Double refraction, called "Formdoppelbrechung," also plays a part in this effect.

Former observers have already pointed out that the regular double refraction phenomena of sperms are very common; it always occurs with longish forms of sperm heads. This is confirmed and quantitatively proved in the thorough and far-reaching recent investigations of E. Pattri. This worker also established the important fact that in spermogenesis the longish, optically negative, doubly refracting head form develops from a swelling-out process. Correspondingly, on the other hand, roundish, optically isotropic formations. This should be thought of as in the case of the artificial swelling of longish sperm heads, their anisotropy goes over into optical isotropy when the formation is rounded off. It is to be assumed that in the case of the spermal round forms the molecules and micelles have a random distribution and therefore an optically compensating effect on each other.

Debye-Scherrer photographs, taken at my request by Dr. G. Boehm, show that the above-mentioned double refraction is not caused by crystalline lattices. Indeed the X-ray effect agrees with assumption

of paracrystallinity.

Thermics.—An especially strong paracrystallinity is to be ascribed to the paracrystalline sperm heads of Sepia officinalis, corresponding to the examples brought forward on page 1016 of artificial liquid crystals which decompose first, instead of going into an isotropic melt. In the case of the above-mentioned sperms this marked paracrystalline strength acts also as a hindrance to a transition into a crystalline modification. This is reminiscent of the very considerable stability of artificially mixed paracrystals.

## (c) Muscles.

Muscle fibres, on account of their optical and X-ray behaviour, are also to be reckoned as paracrystalline materials. While referring the reader to the thorough exposition in W. J. Schmidt's work, Bausteine des Tierkörpers in polarisiertem Lichte, we might briefly note here with regard to the optics that the smooth muscle fibres exhibit clear positive uniaxial double refraction. Their longitudinal direction corresponds to the axis of isotropy. They are imbedded in an isotropic matrix. On contraction of the fibres their double refraction diminishes, which can be explained as a consequence of partial optical compensation of the numerous randomly distributed and indeed deformed micelles.

Stretching increases the optical anisotropy because of the require-

ment of parallelism of the structural parts of the fibre.

The cross-striped muscles develop out of the smooth fibres by subsequent differentiation into sharply delimited, transverse, optically isotropic and anisotropic layers. The latter are optically positive with regard to their longitudinal directions. The axis of isotropy falls in the

<sup>27</sup> E. Pattri, Z. Zellforsch, 16, 723, 1923.

<sup>&</sup>lt;sup>25</sup> On Plate 3, Fig. 1, a photograph of paraazoxybenzoic ethyl ester by D. Vorländer is reproduced for comparison with the sperm optics (Plate 3, Fig. 2). <sup>26</sup> In the photographic original, and therefore in Plate 3, Fig. 2, the delicate appendix does not stand out.

same stretching. Accordingly distorted conoscopic axial pictures are obtained. Von Ebner 28 found the strength of double refraction in the mean to be 0.0021 for the relaxed and 0.0015 for the contracted muscle.

Of the older X-ray studies of the dried material those of R. O. Herzog and W. Jancke <sup>29</sup> may be mentioned here. G. Boehm and K. F. Schotzky <sup>30</sup> succeeded in obtaining clear X-ray pictures of living muscles, by using exposures of only a few minutes to very intense copper Kα-rays. These diagrams reproduce the phenomena with a dried as well as a living relaxed muscle of Rana esculenta (Plate 3, Figs. 4 and 5). The external interference ring seen is due to the water content (about 80 per cent. of the object), the two interference points lying closer inside belong to the bundles of fibres of the muscle. Dried and living muscles do not show appreciably different separations of these points. This implies that there is no marked difference of the micellar structure. The crescent forms which replace the sharp points in the case of contracted living muscles point to a partial deparallelisation and also to a deformation of the micelles. There is no evidence of crystallisation of the muscle on deformation, as for instance in the case of india-rubber.

In addition to these facts, the more recent and also very valuable results of investigations by G. Böhm on stretched myosine threads should be mentioned. The albumen components of the cross-striped skeleton muscles consist, according to H. H. Weber, of about 70 per cent. globulin like myosine and 30 per cent. myogen of albumen nature. A long shape must be ascribed to the globulin molecules as is seen by observations of stream double refraction 31; those of albumen have no marked longitudinality. By squirting into distilled water from a capillary, threads may be obtained from myosin solutions as H. H. Weber showed. They exhibit the possibility of a more than 100 per cent. stretching. In this extended state they show positive double refraction with  $n_y - n_a = \text{approx}$ . 0.006. With X-rays an excellent fibre diagram was obtained, which corresponded completely with that of the Sartorius muscle of Rana esculenta. Thus in myosin preparations we have an excellent model of muscle structure.

#### (d) Nerves.

The optical properties of these formations, also bioparacrystalline, will be only briefly mentioned, the reader being referred to the more extended exposition of W. J. Schmidt (Bausteine des Tierkörpers in polarisiertem Lichte), in which further details of the literature are given. In the case of most complex nerve systems there are three components: (1) a boundary in the form of a tube-shaped external cover; (2) an axial cylinder; (3) the binding tissue surrounding the actual nerve as an intermediate substance. As Ehrenberg recognised in 1849, the boundary is optically anisotropic with  $\alpha$  in the longitudinal direction. The optical axes of the substances lie radially. Thus this direction corresponds to y. It is certainly worthy of notice that such a structure corresponds completely with that of lecithin-myelin sloughs.<sup>32</sup> As one can observe

<sup>28</sup> V. Ebner, Untersuchungen über die Anisotropie organisierter Substanzen

 <sup>&</sup>lt;sup>29</sup> R. O. Herzog und W. Jancke, Naturwissenschaften, 14, 1223, 1926.
 <sup>30</sup> G. Boehm, Kolloid Z., 61, 269, 1932; Z. Biol., 91, 203, 1931; 92, 45, 1931;
 G. Boehm und K. F. Schotzky, Naturw, 18, 282.
 <sup>31</sup> G. Böhm and R. Signer, Helvetica chemica acta, 14, 1370, 1931.
 <sup>32</sup> Schotzky, Naturw, 18, 282.

<sup>32</sup> See F. Rinne, Koll. Z., 60, 288, 1932.

on removing the boundary, by means of alcohol or ether, the interior of the nerve appears to be very weakly optically positive. X-ray investigations of nerves have been made by R. O. Herzog and W. Jancke 33 and most recently by G. Böhm. 34 The last named worker studied nerves of different structure types and so was able to distinguish between the above-mentioned three separate components.

	Binding Tissue, Per Cent.	Regulated Binding Tissue. Per Cent.	Regulated Lipoid. Per Cent.	Axial Cylinder. Per Cent.
Ordinary nerve Olefactory nerve (pike) Scheerennerv (cray fish)	 63 61 ca o ca o	++++	ca 28 O small O	ca 9 39 ca 100 ca 100

The boundary part is characterised by a marked "sickle" diagram in Böhm's photographs. The interference points lie in the direction of the length of the fibre in accordance with the radial structure. The axial cylinder shows no trace of any structure with X-rays. The abovementioned more sensitive optical polarisation method does, however, show a certain amount of distribution of fibrous formations. The binding tissue shows a more or less clear fibrous structure in the direction of extension of the nerve.

### IV. On the Nomenclature of Structural Types.

The application of a thorough classifying principle to the nomenclature of scientific systems and the use of short but clear names has great scientific importance. This is relevant in an exposition of the latest state of knowledge. From an educational point of view a practical nomenclature considerably simplifies the understanding of the fundamental scientific facts. It is clear, therefore, that with the progress of the science, a revision of nomenclature is necessary from time to time in order to replace obsolete terms by more up-to-date ones. In doing so it is also most necessary to take into account the international understanding of the subject.

A survey of nomenclature in the principal groups of matter shows that there is much that could be improved. However, there is some justification for postponing improvements, especially in cases where scientific development is still progressing. Besides, it is no great misfortune that names like "liquid crystals," which might be more suitably replaced, nevertheless remain in use, since they are to a certain extent of historical interest. The replacements necessary from an exact scientific point of view should take place gradually of their own accord.

With regard to nomenclature of fine-structure components, it seems useful to me to supplement the well-chosen German words: "Feinbaulehre" "Feinbauleile," "feinbaulich," Feinbau," with parallel words for international purposes, which derive from "leptos" [= fine, delicate] and lead to the terms: "Leptology," "Leptosomes" (or more briefly, Leptons), "leptonic" and "Leptotaxy." A start in the use of these

<sup>&</sup>lt;sup>33</sup> R. O. Herzog and W. Jancke, Festschr. K. Wilh. Gesellsch. 10-jahr. Jubiläum,
<sup>1921</sup>.
<sup>34</sup> G. Böhm, Kolloid Z. 62, 22, 1933.

names has already been made in the English, American and German literature. In conclusion the international expression "Leptyl" for a fine-structure group seems to be in harmony with the traditional chemical names, Methyl, Ethyl, Aryl, etc.

An acceptable nomenclature for the fine-structural complex types can only be developed on a structural basis. The division of matter into gases, liquids and solids does not accord with this classification. Indeed, all gases have an irregular type of structure, while liquids and gases become identical at the critical point. Further, glassy melts transform very gradually into the solid aggregate state, so that in this case an exact line of demarcation between liquid and solid is impossible. Finally, liquid and solid materials sometimes represent several principal structural types.

From the fine-structural point of view, on the other hand, we have unambiguously the division into

- Ataxy = irregular structure.
- 2. Eutaxy = regular structure.

The name "amorphous" proposed by J. N. Fuchs <sup>35</sup> in 1833 and now in general use is based on remarkably confused considerations. Fuchs ascribes amorphousness (absence of form) to the substances concerned, although, on the other hand, he describes them as the geometrically most complete, "the mother structure" of all forms, the "Unendlicheck," or in other words the sphere as a "substitute of the real underlying form." Fuchs was near the real truth when he described the substances concerned as having "equal properties in all directions." Nowadays the position is that the relevant principle of irregular fine structure is tacitly substituted for the expression "amorphous." Perhaps a systematic replacement will gradually take place, in the above-mentioned manner (Ataxy, atactic substances, Atactites).

The word "crystal" was already distinguished as an expression for fine structurally three-dimensional periodic objects, with the first relevant and competent scientific consideration of the subject, i.e. with the foundation of crystallography by Huygens and Haüy. The figures and discussion given by these workers are exactly equivalent to the later space lattice conception (Text, Figs. 3 and 4). Thus the word crystal indicates in itself, without further description, a space lattice

object.

The X-ray researches by v. Laue, Friedrich and Knipping on crystals provided a brilliant confirmation of the Huygens-Haüy hypothesis.

Paracrystals are closely related to crystals and so justifiably closely related in nomenclature, with their one- or two-dimensionally periodic structure instead of a space lattice.

On the other hand, it would be permissible to define these formations extending the sense as crystal, if the latter word had the general significance of any object with a regular fine structure. Even then, however, it would also be desirable to point out the peculiarities of one-or two-dimensional structures by always adding the prefix "para" in dealing with them.

<sup>&</sup>lt;sup>35</sup> Joh. Nep. Fuchs, Über den Opal und den Zustand der Gestalltosigkeit (Amorphismus), fester Körper. Bayerische Annalen, 1833, N. 51, 345-351. His observations were extended to glasses, resins, rubber, overcooled sulphur melts, etc.

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The expression "liquid crystals" (due to V. Lehmann 36) introduces by the adjective a property which is not typical of the whole material (which may be partly hard or brittle). Besides this "liquid" property, as H. Zocher pointed out, is of an undesirable physical vagueness, from the nomenclature point of view.

The adjective mesomorphous proposed by G. Friedel 37 expresses an intermediate morphology (between amorphous and crystalline), but having regard to the spherical form often occurring with fine-structurally irregular as well as paracrystalline substances, this name is not well suited for an exact description. "Amorphic" and "mesomorphic" have the same morphological characteristic. The systematic classification is according to fine structure, and this the expression "mesomorphic" does not take into account in its construction. The same is true in the case of H. Zocher's suggestion mesophase, 38 inasmuch as the attempt

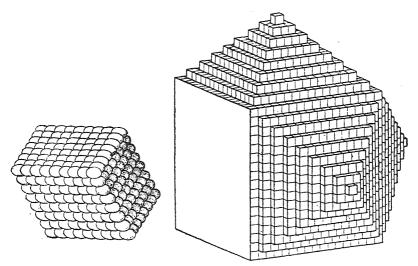


Fig. 3.—Leptology (fine structure) of calcite (Huygens).

Fig. 4.—Leptology (fine structure) of rock salt (Hau).

to give the expression "Phase" a structural meaning has not succeeded. It seems to me, further, that it is better to bring out the natural proximity, as in the names crystal and paracrystal, rather than to emphasise the intermediate nature as above. Random and regular fine structure are separated by a very wide gulf, while paracrystals and crystals are finestructurally similar. They only differ in the degree of their fine-structural regularity.

These considerations lead me to consider the following grouping of fine-structure components and their complex types as the most practical:

<sup>&</sup>lt;sup>36</sup> For a time O. Lehmann used the name "Pseudocrystals" for a certain

group. See Ergebn. d. Physiologie, 16, 286, 1918.

37 G. Friedel, Ann. Physique, 18, 273, 1922; G. and E. Friedel, Z. Krist.,

 $<sup>^{38}</sup>$  See the series of interesting studies by H. Zocher and V. Birstein, Z. f. physik. Chem., 142 A, 1929.

I. Basic material:

Protons and Electrons.

- II. Basic types: Leptons:
  - I. Atoms.
  - 2. Molecules.
- III. Complex types.
  - I. Ataxy.
    Atactites.
  - 2. Eutaxy.
    - (a) Paracrystals.
    - (b) Crystals.

#### V. Conclusion.

I hope that the above experiments and speculations may be regarded from the point of view that was intended, namely, as an attempt to contribute a small share to a more extended and deeper knowledge of the important group which forms the centre of discussion in this paper.

# CRYSTALLINE PHASES OF SOME SUBSTANCES STUDIED AS LIQUID CRYSTALS.

By J. D. Bernal and D. Crowfoot (Cambridge).

Received 29th March, 1933.

It is surprising, in view of the immense amount of labour expended in the study of liquid crystals, how little attention has been paid to the solid crystalline forms of the same substances. This omission, striking enough in the days of classical crystallography, has become all the more glaring now that it is known that even preliminary X-ray analysis of molecular crystals can furnish details on the size and shape of molecules and their mode of aggregation.

Up to the present, the only published work in this field has been that of Kast <sup>1</sup> on single crystals of para-azoxyanisole and K. Herrmann and A. Krummacher <sup>2</sup> on crystal powders, in the course of their extremely valuable X-ray investigation of X-ray diagrams of the mesophases.

In the present work an attempt has been made to derive the crystal structure of a few typical substances which give liquid crystals on melting, and to correlate the data derived from the structure with the optical appearances of the mesophases, and with observations on the nature of mesophase transformations.

The crystals examined were chiefly supplied by K. Herrmann, by V. Freedericksz and Zolina, and by A. S. C. Lawrence, to all of whom we owe our cordial thanks for suggesting the attack on this fascinating problem.

A fairly thorough X-ray study, with oscillation and Weissenberg photographs has been made on the following crystals: (I) Para-azoxyanisole; (2) Para-azoxyphenetole; (3) Anisal I: 5 Diaminonaphthalene; (4) Cholesteryl chloride and bromide. A more qualitative examination has also been made on (5) Dibenzylidinebenzidine, (6) Ethylanisal p-amino cinnamate, and on the metastable forms of (I) and (3).

In most of these cases the measurement of cell size and space group, combined with the determination of the principal optic directions in the crystal and the intensities of the chief X-ray reflections, have sufficed to fix within fairly narrow limits the mutual positions and orientations of the molecules. This was made easier by the discovery of a new phenomenon, characteristic of the crystals of substances which yield mesophases. On most X-ray photographs there appear, besides the sharp points of crystal plane reflections, blurred lines—so-called "smear lines" —which had already been observed in some minerals (mica, asbestos). These lines correspond to a diffuse reflection in certain planes of the reciprocal lattice, the normal to which in the crystal lies always parallel to the molecular length along which there is a certain freedom of translatory movement (see below). From this information the effective size and shape of the molecules in the crystals of these substances can be found, and the inference can be fairly made that this size and shape is retained in its liquid crystal phases.

The detailed results are summarised below. Fuller crystallographic data will be published elsewhere.

The crystallography of this substance has been described (Groth,  $V_{\bullet}$ , p. 72); it occurs in monoclinic prisms along b, bounded by (IOI) and (IOI). The cell dimensions are

$$a = 11.0$$
  $b = 8.10$   $c = 14.95$   $\beta = 107^{\circ}$  30'.

This cell contains four molecules. The reflections of (hol) are absent if k+l is odd, and of (0k0) when k is odd. As there is no evidence of piezoelectricity the space group is  $C_{2h}^5 - P_{21}/n$ . There is no molecular symmetry. The orientation of the molecules follows from the The refractive indices have been measured,3 optical properties.  $\gamma = 2.198$ , yellow with strong absorption,  $\beta = 1.573$ ,  $\alpha = 1.564$  practically colourless and lie nearly  $\perp$  to (001) along b and  $\parallel$  (001) respectively. The length of the molecule is therefore nearly perpendicular to the c face, and the almost uniaxial positive nature of the crystal points to the planes of the rings in the same or different molecules being nearly at right angles. The second hypothesis is accepted provisionally from the analogy with the known structures of the azobenzene-stilbene group.4 It is possible to fit molecules of such orientation into the cell so as to give a plausible structure accounting qualitatively for the chief X-ray intensities. Such an arrangement is shown in Fig. 1.

This interpretation is rendered more certain by the appearances of "smear lines," that is, the drawing out of spots on certain layer lines

<sup>&</sup>lt;sup>3</sup> J. Zadoc Kahn, C.R., 187, 1138, 1927.

<sup>&</sup>lt;sup>4</sup> J. Hengstenberg and H. Mark, Z. Krist, 70, 283, 1929.

perpendicular to this zone. This indicates unequivocally a structure in which the x and y co-ordinates of the molecules are fixed, but where the z co-ordinate is variable. In the case of the micas and asbestos where similar smear lines are observed, the variability is due to variable chemical constitution; here it is almost certainly due to molecular translations along the favoured c direction. These translations need not be active ones due to heat motion, but may simply represent a statistical uncer-

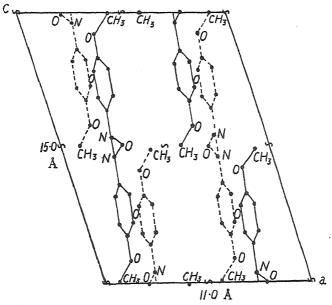


Fig. 1.—p-azoxyanisole projected on the ac plane.

tainty in the z co-ordinates of the molecule, due to an abnormal freedom of motion parallel to the length of the molecule. Two points of interest in the structure may be noted. The molecules do not lie in layers as in most aliphatic and aromatic long molecular structures. Instead they are imbricated, and in such a way that the ether group of one molecule comes nearly in contact with the azoxy group of its neighbour. The significance of this will be discussed below.

#### 1a. para-azoxyanisole, metastable (white).

Attempts were made to take oscillation photographs of single crystals of this form prepared from the melt by rapid cooling and with their transformation delayed by cooling to 5° C. Although definite patterns were obtained, they were not sufficient to establish the cell or space group. The optical examination of the crystals and of their transformation to single crystals of the stable form suffices to show that they differ remarkably little except in habit, being elongated along the direction corresponding to [IOI] in the stable form, instead of along [OIO] and

having the direction of  $\alpha$  along b instead of  $\perp$  to c. The molecules are therefore presumably all parallel, and with their planes nearly at right angles. Nothing, unfortunately, can be said about their relative position, nor any explanation given for the lack of yellow colour.

These crystals, though not isomorphous with the anisole, are built on the same general plan.

The crystals are monoclinic prisms with the following cell dimensions:

$$a = 15.4$$
  $b = 5.41$   $c = 17.6$   $\beta = 94^{\circ}$ .

There are four molecules in the cell. The reflections of (hkl) are absent when h + k + l is odd, and of (h0l) when h or l is odd. This

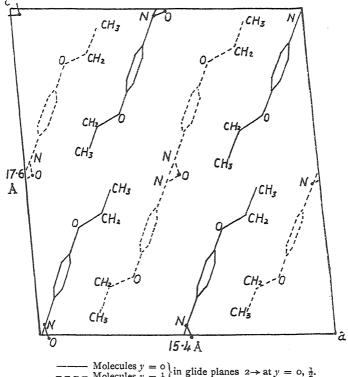


Fig. 2.-p-azoxyphenetole projected on ac face.\*

might indicate molecular symmetry, but an examination by Dr. Wooster of the piezoelectric properties showed a large effect, so that the crystals are probably monoclinic domatic of space group  $C_s^4 - Ia$ .

<sup>\*</sup> In the figure the molecules have incorrectly been drawn along the [IOI] instead of the [IO2] but this does not affect the general arrangement.

The optical properties are those of a strongly positive nearly uniaxial crystal with the principal axes  $\gamma$  nearly parallel to the direction [ $\overline{102}$ ]. As (402) and (202) are the strongest X-ray reflections, the axes of the molecules almost certainly lie between [ $\overline{102}$ ] and [ $\overline{001}$ ]. This is supported by the smear lines which also correspond to the zone [ $\overline{102}$ ]. A structure built on these lines is shown in Fig. 2. (See footnote, p. 1035.)

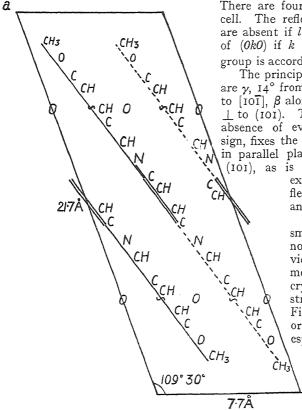
As in para-azoxyanisol, the molecules are imbricated, and the ether groups of one molecule lie next to the azoxy groups of the next.

### 3. Anisal 1:5 diaminonaphthalene.

$$CH_3O$$
— $CH=N$ — $N=CH$ — $OCH_3$ .

3a. Stable Form (from solution).—Occurs in monoclinic plates flattened along b and elongated along a. The cell dimensions are

$$a = 21.7$$
  $b = 12.7$   $c = 7.7$   $\beta = 119^{\circ}$  30'.



Screw axes.

O Centres of symmetry  $y = \frac{1}{4}$ ,  $\frac{3}{4}$ . Shown in italics between the chains.

Naphthalene neucleus.

----- Carbon chain y = -1.2a.

Carbon chain y = +1.2a.

Only the two lower molecules in the cell are shown, the others can be theory, to a derived by the screw axes.

Fig. 3a.—Anisal 1:5 diamino naphthalene. Projected on ac face.

There are four molecules in the cell. The reflections from (h0l) are absent if l is odd, and those of (0k0) if k is odd, the space group is accordingly  $C_{2h}^5 - P_{21}/c$ .

The principal optic directions are  $\gamma$ , 14° from c, nearly parallel to [101],  $\beta$  along b and  $\alpha$  nearly  $\perp$  to (101). This, even in the absence of evidence as to the sign, fixes the molecules as lying in parallel planes not far from (101), as is confirmed by the

extremely strong reflections from (202) and (002).

There are nosmear lines. This is
not surprising in
view of the high
melting-point of the
crystals. A probable
structure is shown in
Figs. 3a and b. In
order to fit the cell,
especially the short baxis, the mole-

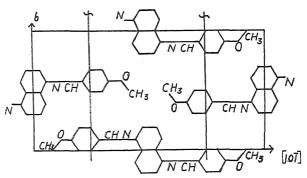
cules must be considerably interlocked, as shown. Such a structure would not correspond, on the author's theory, to a liquid crystal phase, but the

structure which physically corresponds to the liquid is the meta-meta-stable form 3c.

3b and 3c.—When Anisal I:5 diaminonaphthalene is crystallised rapidly from the nematic melt, the white meta-metastable form, 3c,

appears; few after this minutes either transforms to the white stable form. 3a, or more often to the yellow meta- N stable form, 3b, which in turn, often not until after many hours, transforms to 3a.

X-ray photographs were obtained of all these forms, but



Only one layer of molecules is shown.

screw axes.

Fig. 3b.—Anisal 1.5 diamino naphthalene. Projected on (101) plane.

as even in the minutest crystals there appeared in the course of exposure crystals of one of the other forms, considerable caution is needed in the interpretation of the photographs.

The following facts, though incomplete, are fairly well established. The most direct basis of comparison are the reflections of the principal plane b (O10) in the stable form. The spacings and orders of intensity of this plane are shown below:

$$3a$$
  $b = 12.7$  Å 010 abs. 020 vs. 030 abs. 040 ms.  $3b$  " $b$ " = 11.4 010 ms. 020 abs. 030 s.  $3c$  " $b$ " = 13.1 010 abs. 020 m. 030 abs. 040 vs.

In addition, there is a primitive translation in 3b of 9.25 Å, not  $\perp$  to "b," which indicates that b cannot here be a diad axis, and that the crystal may indeed be triclinic.

It is noticeable that the two "white" forms, 3a and 3c, resemble each other far more closely than either does the intermediate "yellow" 3b.

The optical examination of the transformation indicates that both transformations  $3c \to 3b$ ,  $3b \to 3a$  and  $3c \to 3a$ , particularly the last, are of a very slight nature as recrystallisation is regular, with only slight change of optic directions, that of  $\beta$  remaining in all cases nearly perpendicular to the principal "b" plane. This indicates only a slight degree of geometrical rearrangement of the molecules without loss of parallelism. It is reasonable to assume that this will hold even in the liquid crystal phase.

# 4. Cholesteryl chloride and bromide. Br

These isomorphous structures were examined primarily in an attempt to elucidate details of the inner structure of cholesterol molecules, but it was noticed that the photographs showed marked smear lines and optical examination of the melt showed all the typical cholesteric structures, including the beautiful iridescent colours. It is interesting to compare these structures with those of the above substances, which only give nematic mesophases.

The crystals are lath shaped monoclinic, elongated along b with only the (001) face prominently developed.

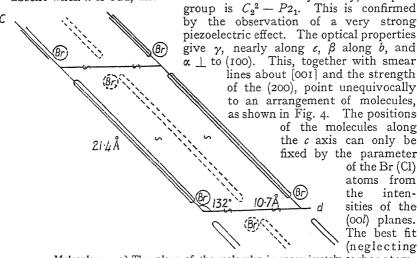
The cell dimensions are

Chloride 
$$a = 10.3$$
  $b = 7.0$   $c = 21.2$   $\beta = 131^{\circ}$   $a \sin \beta = 7.8$   
Bromide  $a = 10.7$   $b = 7.45$   $c = 21.4$   $\beta = 132^{\circ}$   $a \sin \beta = 7.9$   
 $= 2$  molecular thickness.

These are typical cholesteric dimensions,—compare the orthorhombic dibromocholesteryl chloride  $a=8.07,\ b=7.7,\ c=2\times21$ ,—with a flat molecule

$$3.95 \times 7.45 \times 21.4 \text{ Å}.$$

There are two molecules in the cell. The reflections of (0k0) are absent when k is odd, and as there is no molecular symmetry, the space



Molecule y = 0 The plane of the molecules is approximately carbon atoms = = = = M Molecule  $y = \frac{1}{2}$  perpendicular to the plane of projection. entirely in Fig. 4.—Cholesteryl bromide projected on ac plane. the higher

the higher orders) is ob-

tained at z = 0.07c, indicating Br atoms in layers 2.8 Å apart, so that there is no appreciable imbrication in this case. The possible significance of this will be discussed later.

#### 5. Dibenzylidenebenzidine.

This, unlike the other substances examined, crystallised in the typical thin flakes of a long molecule compound. The crystals were extremely imperfect, and the X-ray data correspondingly doubtful. The dimensions are probably correct, but the space group uncertain, and may be only a pseudo-space group. The data are a=5.9, b=7.7,  $c\sin\beta=21.5$  (main spacing); the  $\beta$  angle is uncertain, probably 115°, giving c=23.8 Å, against a calculated molecular length of 20 Å, which would allow 3.8 Å for end clearance. There are 2 molecules per cell, the space group is prob-

ably  $C_{2k}^5 - P_{21}/a$ , giving molecules with centres of symmetry at (000)  $(\frac{1}{22}0)$ . The inclination of the molecules is probably with the long direction along c. The optical properties were  $\alpha$  along b,  $\beta \perp$  to (100),  $\gamma$  along c. The optic axial angle was small. This points to the planes of the molecule being inclined to each other, much as in para-azoxyanisole, but more nearly parallel to the (010) planes. In this case, also, the molecules are in layers, and there is no imbrication.

### 6. Ethyl Anisal p-amino-cinnamate.

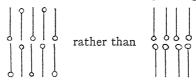
The crystals of this substance consisted of extremely thin monoclinic flakes somewhat elongated in the  $\alpha$  direction and much twinned. They were strongly optically positive with y nearly parallel to c and  $\alpha$  along b.

The cell dimensions were approximately

$$a = 6.65$$
  $b = 7.88$   $c = 45.6$   $\beta = 135^{\circ} 35'$ 

(0k0) was absent with k odd and (hol) with l odd the space group is accordingly  $ac_{2h}^5 - P2_1/c$ . There are four molecules per cell.

The most plausible explanation of this structure is that of a normal long chain layer crystal. The molecules must lie nearly along the c axis, therefore inclined at 45° to the c plane, the calculated molecular length 20 Å agreeing well with the half c axial length 22.8 Å. The molecules lie in two layers related by a glide plane gliding in the c direction. This double layer differs from that of acids, alcohols and salts in that in each layer there are molecules pointing in both directions



Dimensions and optical properties suggest that the planes of the rings are not more than  $35^{\circ}$  from the b planes. The whole structure is typically that of a substance with long molecules arranged in layers and contrasts with the interleaved character of p-azoxyanisole.

It is regrettable that, for lack of suitable crystals, these were the only X-ray examinations made of crystals yielding smectic mesophases. However, this defect is to a certain extent removed by our knowledge of the optical properties of such crystals, suggesting similarities to those of known structure, and by K. Herrmann and Krummacher's 2 observations on powders. Both lead to the conclusion that all these crystals are typical layer crystals of the aliphatic or aromatic long molecule type, having single or double layers of parallel molecules. The transition from smectic to solid phase referred to below makes this almost certain.

#### Optical Observations.

The value of the X-ray determination of crystal structure of substances giving rise to mesophases is small unless it can be correlated to

some of the more striking properties of the mesophases themselves. This might have been done by studying published work, but the observations recorded were so various that it was considered worth while to make fresh ones on the actual substances examined by X-rays.

For this purpose use was made of a hot wire apparatus originally made for the production of single crystals of organic substances from melts. Though plainly it must be used as complementary to the hot stage apparatus, it has several advantages that the older method does not possess.

The apparatus is ideally simple. It consists in a movable stage across the central aperture of which is stretched a nichrome wire, which can

be heated by current from an accumulator.

The specimen is melted by a small flame between a microscope cover glass and a splinter of cover glass about 10 mm. long, 1 mm. wide at one end, and tapering to a needle point. When the specimen is placed on the microscope stage under the heated wire, which is adjusted to touch the top glass, there is a sharp temperature gradient which may include 100° C. (more or less according to the temperature of the wire), in the width of the field, and in which all the phases of the substance can be simultaneously viewed in equilibrium. Transformations are observed, not by heating the wire, but by moving the specimen very slowly, and therefore heating one side and cooling the other. Metastable phases can be induced by overheating one end of the specimen and then moving it rapidly away from the wire, and in this way can be observed in equilibrium with the melt. See Fig.

By destroying all but one nucleus in the narrow end and crystallising slowly from that, it is possible to obtain large single crystals of stable or metastable forms, and even large oriented plates, smectic or nematic. Similar observation could be made in a wedge-shaped split mica plate or on glass or crystalline surfaces without covers. The chief advantage of the method is that different phases can be studied simultaneously, and their mutual relations far more easily determined than by the ordinary method. Its chief disadvantage is that it gives no exact temperature measurements, but rough measurements can be obtained by calibrating the temperature gradient by observation of the

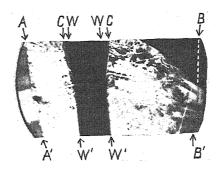
position of known transformation.

The following is a summary of the significant observations:—

(I) Para-azoxyanisole.—Observations of melts were made on glass and mica. In both cases large oriented plates of the nematic phase were found, showing all the well-known phenomena: singular lines, nuclei of various sorts, etc., but it was noticed that these singularities arose either from too rapid temperature change or from irregularities in the glass or mica. Both the stable (yellow) and metastable (white) form could be produced at will and, by arranging them on opposite sides of the hot wire, the melting-point of the latter could be determined to be 84° C., using the melting-point of the former (94° C.) and of the nematic-liquid transformation (150° C.) as fixed points (see Plate 1).

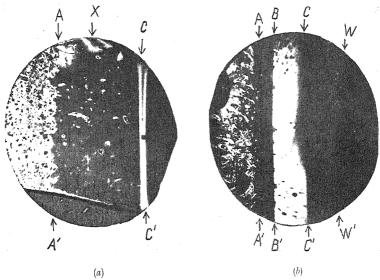
It was soon apparent that the metastable form was far more closely related to the nematic than was the stable form. This showed particularly well on mica. Here, both the nematic and metastable forms tended to be oriented, the a axis of the latter making 40° to the b of mica. Under these conditions, the optical properties of the metastable form, and the nematic were extremely similar, only amounting to a fraction of a fringe in birefringence, so that the crystal boundary was

 $\begin{array}{lll} \textbf{PLATE} & \textbf{1.} - p\textbf{-azoxyanisole.} - \textbf{Nematic} & phase & in & equilibrium & with & isotropic \\ & liquid & with & metastable & phase & (on & right) & and & stable & phase & (on & left). \\ \end{array}$ 



WWW'W' marks shadow of hot wire. CC edge between isotropic liquid and nematic phase. AA' and BB' are the edges of the stable and metastable crystals respectively. The edge BB' is difficult to see owing to the homeomorphous transformation between solid and liquid crystals. The nematic phase has a temperature interval of stability AC against the stable phase and BC against the metastable.

[To face page 1040.



2(a) shows the substance between glass; 2(b) between mica plates.

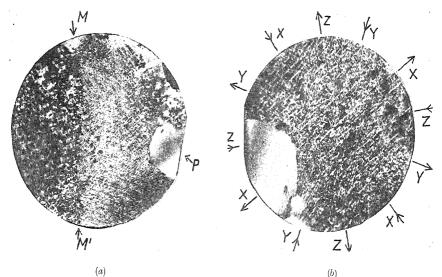
WW' is the shadow of the wire (out of the field to the right in 2(a)).

AA' is the boundary of the smeetic and nematic phases. CC' is the boundary of the nematic and isotropic phases.

BB', which appears in 2(b) only is the boundary between the homeotropic nematic phase AB and the parallel oriented nematic phase BC.

In 2(a) no distinction can be seen; the whole region AC is homeotropic, except in the region X where the traces of coloured bands of parallel orientation can be seen.

PLATE 3.—Ethylphenylbenzylamino-cinnamate on mica.



3(a) shows the metastable crystals to the right of MM', the slowly growing stable form to the left. To the extreme right a patch of crystals with axes parallel to the mica can be seen.

 $\mathfrak{Z}(b)$  shows an enlarged portion of  $\mathfrak{Z}(a)$ . The pseudo hexagonal interpenetrating network can be seen. The principal directions of the triple system of crystals are shown by the arrows XYZ. Owing to the position of the nicols X and Y show bright, Z dark.

often hard to distinguish. The conclusion is almost forced that, at the melting-point, the molecules do not even change the gross nature of packing or orientation but, remaining parallel, acquire a possibility of transitional movement. The stable form, on the other hand, stands out in marked contrast to the liquid. Both forms show the persistence of the orienting pellicle on glass or mica after fusion, but the edge of this is almost invisible in the case of the metastable crystals. The pellicle can be observed to fuse below the nematic-liquid transition, but it is interesting to note that under no circumstances have the pellicular pseudo crystals been observed to grow.

- (2) Para-azoxyphenetole behaves in most respects like para-azoxy-anisole. Some specimens only, apparently contaminated with para-azophenetole, showed a metastable form, and the stable form behaved towards the liquid very much as did the stable form of para-azoxyanisol.
  - (3) Anisal 1:5 Diaminonaphthaline.—This substance, apart from its higher melting-point, did not behave very differently from anisole or phenetole. However, besides the white meta-metastable form, 3c, presumably corresponding to the nematic phase, and the yellow metastable form, 3b, there is the white stable form, 3a, all of which could be observed in equilibrium with the nematic phase. The interest of this substance lies in the extreme width as well as length of its molecule, which suggests the possibility that, unlike the para-azoxyanisole and phenetole, two orientations in the molecule are fixed in the nematic phase. This is supported by the crystal structure, and by Hermann's observation that the X-ray pattern of the nematic phase in a magnetic field shows two halos of different spacing at right angles. It was, however, found impossible to obtain optical evidence for or against this hypothesis, as no optic figure could be observed.
  - (4) Cholesteryl Chloride and Bromide.—These isomorphous bodies were examined by the hot wire method. Both show cholesteric phases, but these are metastable, or, more correctly, meta-metastable, and only appear on cooling. There are stable and metastable crystalline forms, both with melting-points higher than the cholesteric, so that neither can be considered as corresponding to it in inner structure.
  - (5) Dibenzylidenebenzidine.—This showed a typical nematic mesophase, orientated perpendicular to the glass. The only unusual observation is that drops of this solidifying showed typical layers of Grandjean in the solid. This, and similar observations on mica, where the nematic phase and the crystals show orientation, suggest that in this case there may be a smectic phase, so isomorphous with the crystal that no line of demarcation can be observed. If this is so, the absence of cones shows that it must be of the SI or solid smectic type (see below).

### (6) Ethylanisal paraaminocinnamate

$$CH_3O$$
— $CH$ = $N$ — $CH$ = $CH$ — $CH_5$ 
 $\parallel$ 
 $O$ 

The examination of this substance was repeated since the original communication in advance Proof at the meeting, in order to clear up the

difference between our previous observations and those of Vorländer. His scheme is shown below:

Liq. 
$$\rightleftharpoons$$
 Liq. cryst. I  $\rightleftharpoons$  Liq. cryst. II  $\rightleftharpoons$  Liq. cryst. III  $\rightleftharpoons$  Crystal I  $\rightleftharpoons$  Crystal II.

Our observations are now completely in agreement with his. We had previously failed to observe the transition  $II \rightleftharpoons III$  which is only visible as a slight alteration in the smectic phase for thicker preparations than we had at first used.

The difference between these phases seems similar to those existing between the smectic phases of the other compounds in that II shows "gouttes à gradins" and III. "gouttes à facettes."

The metastable crystals I which grew slowly in the body of the smectic phase III sometimes appeared to melt again into liquid crystal III, but more often they transformed into the stable crystal II which melted to the smectic liquid II.

Between glass plates this had the usual cone structure while I was homeotropic (see Plate 2a). Between mica and glass large oriented crystalline plates of both I, II and III could be obtained strictly parallel and differing only in the greater birefringence of II. Here III was indistinguishable. In a cleavage of mica the appearance is strikingly different (see Plate 2b). At first sight there appear to be four phases as before, the chief difference being that the second phase is oriented perpendicular to the mica. Closer examination shows that this phase is really double and that there are five in all

Crystals II 
$$\rightleftharpoons$$
 II  $\rightleftharpoons$  I'  $\rightleftharpoons$  I  $\rightleftharpoons$  liquid inclined to  $\bot$  to  $\bot$  to  $/\!\!\!/$  to mica mica mica

I' and II are distinguished by a fine line of division but are absolutely distinct as smectic rods and cones only appear in II while I' shows the typical flashes and Brownian scintillation of nematic phases. As there is no trace of the I'  $\rightleftharpoons$  I division on glass it would appear it is due to the orienting power of mica being a function of the temperature, and here again we would have two textures rather than two phases in the nematic state

The following substances were also observed by the hot wire method, although it was impossible to obtain large enough single crystals for X-ray analysis. The object here was partly to elucidate K. Herrmann's X-ray measurements and partly in an attempt to throw fresh light on the controversy as to the simple or multiple nature of smectic and nematic phases.

## (7) Ethyl-phenyl benzylamino cinnamate.

$$CH=N-CH=CH-C-O-C_2H_5.$$

This substance is stated to occur in four meso forms

An examination with the hot wire verified all these transformations except that from II to III at  $205^{\circ}$  which could not be observed with certainty. Observations were made (a) in drops on glass and mica, (b) between cleavages of mica, (c) between glass and mica cleavage, (d) between glass slips. The results are shown in the Table and in Plate 3a and 3b. In this way different orientations of the phases could be

Phase.	I.	II.	111.	IV.	Crystal I. Metastable.	Crystal II. Stable.
(a) Drops on glass and mica.	Mobile liquid with threads, etc.	Beaded drops sometimes with Grand- jean planes.	Very similar to II but possibly less mobility.	Facetted drops and greater rigidity than II or III.	On cooling appears in hexagonal pattern of biaxial crystals.	Plates slowly replacing I. Melts directly to IV.
(b) Between mica cleavages.	Mobile liquid. Homeotropic.	Mostly homeo- tropic but with a few cones.	Indistinguishable from II.	When homeo- tropic indistinguish- able from II or III.	On cooling quickly, hexagonal pattern. More slowly it appears in nearly uniaxial plates.	Rhombic biaxial plates growing slowly in I.
(c) Between mica and glass.	Oriented parallel to mica.	Oriented parallel to mica.	Indistinguish- able from II.	All oriented parallel to mica and very difficult to distinguish.		
(d) Between glass slips.	Homeotropic.	Cone structure mobile	Indistinguishable from II.	On cooling: cone structure partly effaced very fine striations. On heating: Fine cracks appear in crystals but cone structure is not developed.	basal planes distorted along Dupin's cycloids.	Heavy darkening cracking and distortion of crystals.

observed. Phase I is undoubtedly nematic, setting in homeotropic orientation except in case c where the molecules are parallel to the glass. In this orientation its transition to II shows parallel orientation but markedly lower birefringence. Phases II and III, if, indeed, two separate forms are present, showed all typically smectic characters; Grandjean planes with mobile edges, beaded drops, etc. IV on the other hand is easily distinguishable by its darker colour and the formation of facetted drops as well as by a highly viscous almost pasty consistency. It seems to have no proper structure of its own and appears very different if produced by heating from the stable crystalline phase or by cooling from III. In both cases the general appearance of the previous phase is retained but the crystals appear cracked and the cones fixed in position and with less definite outline. It can be cooled far below 145° C. but at about 110° it transforms very sharply without a trace of undercooling to a metastable crystalline phase whose existence is not previously recorded. This transformation can only be seen easily in orientations perpendicular to the surface. Here the crystals appear as nearly uniaxial and in a characteristic pattern of intersecting lines in six directions 30° apart. This pattern consists of three sets of interpenetrating twins inclined at angles of 120°. Each set contains positive biaxial crystals of small optic axial angle set growing along two directions at right angles (see Plate 3).

The stable crystalline form appears in rhombic plates also nearly uniaxial positive but with larger optic axial angle than the metastable. These grow slowly in the metastable form at room temperature taking several hours to replace it.

The chief interest in these observations is in respect to the nature of phase IV. It is quite clearly different from phases III and from the crystalline phases I and II, but is it strictly a liquid crystal phase? It is certainly not a smectic phase in the ordinary sense since K. Herrmann's 2 X-ray investigations gives not only a series of orders of reflection corresponding to a long spacing of 24.2 Å a number of other sharp lines corresponding to spacings, 5·1, 4·62, 4·42 Å etc., indicating further regularity of structure. He interprets this as due to a new form in which the molecules in the layers are arranged in a definite lattice but in which these layers have no relation to each other. This would correspond to one of C. Herrmann's 5 theoretically possible intermediate states P<sub>0</sub>P<sub>0</sub>R. An alternative explanation is suggested by the hexagonal pattern of the metastable crystals formed from phase IV. The sharp nature of the transformation precludes serious molecular rearrangement and suggests strongly that before breaking up the previously existing arrangement was hexagonal.

The whole phenomenon is extraordinarily similar to that observed by the author for Dodecyl alcohol <sup>6</sup> where a definitely hexagonal form due to rotating molecules was stable just below the freezing-point of the liquid and broke up into plates of the monoclinic form, low temperature, forming a similar pattern to that produced on cooling phase IV.

Phase IV may be in reality a rotating molecule crystalline phase of this type. Such phases are highly deformable and difficult to distinguish physically from liquids, while the hexagonal outlines observed in the alcohol could not be formed as the phase cannot here originate from an isotropic liquid.

This view may not ultimately be in conflict with that of K. Herrmann as the hexagonal planes may be in motion, but further experimental work is clearly needed here.

## 8. Diethyl para xylylidene-bisaminocinnamate.

shows even more interesting phenomena. There are again four alleged mesophases

$$\begin{array}{c} \text{Liquid Crystal} \\ \text{Cryst} \rightleftharpoons \text{IV} \rightleftharpoons \text{III} \rightleftharpoons \text{II} \rightleftharpoons \text{I} \rightleftharpoons \text{Isotropic Liq.} \\ \text{134}^{\circ} \quad \text{168}^{\circ} \quad \text{?} \quad \text{280}^{\circ} > \text{300}^{\circ} \end{array}$$

Of these forms only one, I, is nematic. The other three are certainly not so, as II already shows drops with layers "gouttes à gradins." III and IV can be easily distinguished by the yellow colour of III while IV and II show black between crossed nicols owing to homeotropy.

<sup>&</sup>lt;sup>5</sup> Z. Krist, 79, 186, 1931. 
<sup>6</sup> Bernal, Z. Krist, 83, 153, 1932.

The other distinction is the appearance of the layers which are mobile in II, much multiplied but still mobile in III and acquire irregular outlines in IV. The differences between IV, III and II always occur at the same temperature, but there is no sharp optical boundary such as separates I and II. From Friedel's point of view they might represent the same phase with different textures. The chief difficulty is to explain the yellow colour of III which would seem to indicate inclined molecules, but this is in turn difficult to reconcile with the existence of layer drops. The crystals were found to exist in two forms, one with high double refraction which is metastable and one with small double refraction showing an optic picture with small optic axial angle normal to the main plane. The metastable crystals have a melting-point not more than a few degrees below the stable form, and the rate of transformation is slow especially on mica which seems to favour this modification. As before while II can be accepted as a genuine smectic phase the explanation of III and IV offer the same difficulties as were discussed in the case of (6). Here K. Herrmann's results are peculiarly interesting. He finds sharp side spacings in IV but not in III, and the following main spacings, crystal 39Å, IV and III 32.8Å.

Now the length of the molecule assumed nearly linear between terminal carbons is approximately 33Å which, allowing for an intermolecular —CH<sub>3</sub>, CH<sub>3</sub>— end clearance of 4Å, makes it appear very probable that the molecules lie almost perpendicular to the planes in the crystalline form and must certainly be inclined to them in states III and IV. A double layer inclined structure is extremely improbable in the first instance owing to the nearly uniaxial character of the crystals, while an inclined structure for III and IV is the more probable as shown by K. Herrmann's paper at the present meeting where he has established its existence in the case of other smectic states.

#### Conclusions.

After an examination of such extremely complex phenomena, it is worth while to attempt to bring together the contributions that X-ray and crystal optical studies have to make on the constitution of liquid crystals. This approach is essentially different from that based on observations of properties such as viscosity, orientation, electric and magnetic fields, in that it is concerned with the molecule itself and its immediate neighbours rather than with "cybotactic groups" or "swarms" containing thousands of molecules. In other words it deals rather with the structure than the texture of liquid crystals. The properties of liquid crystals in the bulk are, so to speak, hydrodynamic (electro-magneto dynamic) consequences of the immediate forces between molecules.

Now these cannot be very different in the solid and in the liquid crystal, as the gentle nature of the transformations between them shows. The difference will not be in the state of the field surrounding the individual molecule, but in its possibility of transformation from one such state to a similar one, and the height of the energy barrier then crossed, in other words in the molecular degrees of freedom. C. Hermann has given a complete treatment of the geometrically possible cases, pointing out that at the time (apart from the true liquid (SSS) where every translatory and rotatory movement is possible and the true crystal  $\{(RD)(RD)(RD)\}$ , where none is) there were known the nematic state (SSS)  $C\infty$ , where only one rotational freedom remained, and the

smectic state (SSR) C∞, where only two translations and one rotation are possible. Since then, the work of K. Herrmann has demonstrated in the S I forms of Diethylparaxylylidenebisamino-cinnamate and Ethylphenylbenzylamino-cinnamate, one or both of the types  $P_0P_0R$  or RD(RD)where the sheets, but not individual molecules, have two degrees of translatory freedom and possibly one of rotatory. Lastly, the present work has indicated the possibility of RRD where the rows of molecules have one degree of freedom. There remain the cholesteric phases of which the precise form of association has yet to be discovered. If sufficient substances were examined, further Hermann types, such as RDS, would probably be found.

Now, geometrically, there is nothing to prevent other than spherical molecules from existing in any of these phases, and that they all do not do so is no doubt due to the fact that their domains of stability are included in each other, so that most of these phases would be metastable and monotropic.

With these ideas in mind, we can enquire as to the nature of the molecules required to form liquid crystals. The following conditions are indicative for liquid crystals, though in our present state of knowledge they cannot be considered necessary or sufficient.

1. We may accept to start with the classical postulate that the molecule must be geometrically anisotropic, either rod-shaped, flat, or lath-shaped. Optical (electric, magnetic) anisotropy is, of course, fortuitous, and has nothing to do with the occurrence of liquid crystals, though it profoundly affects their appearance and properties.

2. The molecule must not contain more than one active group (active, that is, in producing intense local electric field) (hydroxy-, carboxy-group) or the melting-point will be raised above the range of stability of the liquid crystal phase. Molecules with only one active group (e.g., soaps) can associate in pairs and thus simulate inactive molecules.

otherwise the unspecific van der Waals' attraction will lower the stability range of the true liquid till it meets that of the crystal. Hydrocarbons do not give good liquid crystals except in some cases for a degree or two above the melting-point. 6 If only one active group is present, or two symmetrically, at the ends of molecules the tendency will be for crystals of the platy, layer type (e.g., Ammonium oleate, ethyl para-azoxybenzoate) which will give a smectic type of liquid crystals. Such crystals might be called "Smectogenic." On the other hand, if molecules contain active groups near the middle, as well as at the ends, this will lead to imbricated crystal structures such as that of anisole or phenetole melting directly to a nematic liquid. Such crystals showing marked smear lines in X-ray photographs might be called "Nematogenic." It is noticeable that ethers tend to give nematogenic, esters smectogenic crystals.

4. The reason for the appearance of cholesteric properties is still obscure, but we may hope for some advance now that the structure of the chemical molecule has been elucidated.7 The most significant

<sup>&</sup>lt;sup>6</sup> See Muller, Proc. Roy. Soc., 138A, 514, 1932.

<sup>&</sup>lt;sup>7</sup> Rosenheim and King, J. Soc. Chem. Ind., 51, 464, 1932.

property of these substances is their optically negative character. This strongly suggests that here we have molecules which are either perpendicular to, or make a large angle with the axis of orientation of the liquid crystals. This is what might be expected of the broad, almost flat, sterol molecule. A geometrical consequence of this is however, the existence of planes perpendicular to this dimension giving a formal resemblance to a smectic phase. Physically, it would differ, however, owing to the fact that the molecules in each layer would not be bound side by side nearly so well, and it consequently has a greater fluidity than the true smectic phase. The small cone structure of cholesteric substances strongly suggests the similarity to the smectic layer structure distorted by surface forces. The most characteristic property of cholesteric liquids, their optical activity, is probably structurally irrelevant, but the optical colour properties, formally a consequence of layer structures of the order of 500-5000 molecules thick, seem to be of fundamental importance. From its scale, however, it seems not to be paralleled by crystal lattice structure, but by the secondary coarser structure of Tamman and Zwicky. It is therefore, in a strict sense, to be interpreted macroscopically by some hydrodynamic theory.

It is probable that all the inner structures observed in mesophases have their origin in surface forces. The effects of these are actually simplest when the surface is that of a rigid foreign substance, glass or mica. If there is free surface in contact with another phase the orientation of molecules inside this surface will be conditioned only by the orientation of the surface layers. In nematic crystals, where there is only orientation and no alignment, the case is simplest. The molecules at the surface will everywhere lie parallel to it, and those in the interior will have to accommodate themselves. In cases where the phase is produced by the confluence of drops, parts of their common surfaces become incorporated in the mass of the liquid. The whole of the nematic phenomena of threads, nuclei of different orders, can be explained extremely simply on this view, but we have no space to go into this question here.

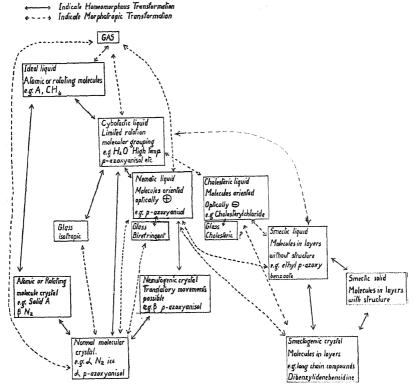
In the case of smectic structures, it is probable that the focal cones, rods, etc., are due to the instability of the plane molecular sheets, devoid of any rigidity against the action of surface tension forces, which must be widely different along and perpendicular to the sheets. The structures will be very different from the nematic, as there can here be no yield by transference of molecules from one layer to another. The smectic state is more influenced by surface forces than any other. In the more fluid nematic and liquid these are limited in their action to a thin layer by the fluidity of the interior; in the solid, they are also limited to a thick layer by the rigidity. Only in the smectic phase does the action of surface forces permeate the whole body of the substance.

After the question of the occurrence and stability of mesophases, the question of the nature of the transformations between them is of the greatest interest. X-ray and optical observations have thrown considerable light on this problem. We may begin by drawing a new distinction between two different modes, "Homeomorphous" and "Morphotropic," of interphase transformations. The chief characters of these are shown in the table.

We may call "Homeomorphous" any transformation between two phases of the same or different kinds (solid, liquid or mesophase) when no change is made in the orientation and little in the mutual positions of the molecules. Such a change is that occurring in the melting of solid argon or copper (simple close-packed solid to close-packed liquid), of that of metastable para-azoxyanisole to the nematic phase, or between crystal I and liq. crystal III in (6) or (7). In this case, there is little change in many of the properties, and we may correctly infer the structure of the higher temperature phase from that of the lower.

In the second or "Morphotropic" type of transformation the mutual arrangement of the molecules is completely altered. Effectively there is superposed on the normal increase in degrees of freedom on melting a polymorphic transformation. This shows itself in abrupt change of properties on melting, changes of volume and of refractive indices, by a

TABLE II.



large latent heat, a relatively high melting-point and by a pronounced tendency to undercooling. In this case the crystal growing in the melt behaves much as if it were coming from solution. Such morphotropic melts are shown by bismuth and ice for example, and in our case by stable p-azoxyanisole and cholesteryl bromide. In cases of melting of this sort we can only infer that the inner molecular constitution of the liquid will be different from the solid and not as in the first what it will be.

A solid will melt morphotropically when its molecular arrangement is such that more than a slight change of mutual molecular position greatly increases the potential energy. This will occur when the forces holding the crystal together are due to local electropolar groups =0, OH, COOH NH<sub>2</sub>, etc., particularly if these are well separated in space. In the case of metalloidal substances, directed valencies fulfil this function. In the extreme cases, the increase in energy on molecular displacement is

so great that no liquid at all is formed as in arsenic or quinone.

Ideally, every liquid has a homeomorphic crystalline phase of which it is the disordered representation, while only certain crystals will have a homeomorphic liquid. In actuality the homeomorphic crystalline phase may often be metastable, monotropic and therefore difficult to obtain or even not be physically realisable, either because before it is reached the molecular movements become so sluggish that a glass results, or when the liquid spontaneously transforms on cooling to another liquid with a different form of molecular grouping. This change can happen gradually, as in the case of water which as is shown in a later paper goes over to an ice-like form, or sharp as in the case of several liquid crystal transformations. Taking these possibilities into account, a scheme can be drawn up showing the main types of transformation possible in solid liquid and mesophases.

From this scheme it can be seen that the mesophases, far from being an anomalous manifestation, take their place in a regular procession from the disorder of the ideal liquid to the regularity of the ideal crystal.

In conclusion it is urged that the study of liquid crystals has reached a stage when isolated research may often lead to more confusion than knowledge, and we express the hope that some scheme of co-ordination of the various methods of attack (optical, X-ray, magnetic, etc.) might be reached at the present conference.

We owe our thanks to the Royal Society and to the Company of Goldsmiths, through whose grants much of the apparatus used in the present research was obtained.

# NOTE ON THE PSEUDO-CRYSTALLINE STRUCTURE OF WATER.\*

By R. H. Fowler and J. D. Bernal.

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The more water is studied, the more anomalous do its physical properties appear. Not only that, but the very existence of water is itself anomalous, contrasting with the gaseous nature of other hydrides, CH<sub>4</sub>, PH<sub>3</sub>, SH<sub>2</sub>, HCl, far more than do even its nearest neighbours NH<sub>3</sub> and HF. The reason for this has been sought in polymerisation, but this has not proved a satisfactory line of attack. From a more modern point of view the explanation of the physical properties of a liquid, quite as much as a crystal, must be sought in the geometrical and physical relations between its constituent molecules, atoms or ions. The present theory of water is based on two facts: (a) That water is not an

<sup>\*</sup> This is a brief account of the chief conclusions of a theory of water and ionic solutions to be published in full in the *Journal of Chemical Physics*.

ideal close-packed liquid, such as mercury or liquid methane. (b) That

the water molecule is known to be assymetrical H+ H+ not HOH.

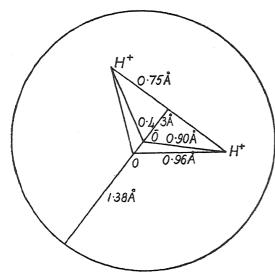


Fig. 1a.—The water molecule model. H+H+ are the hydrogen nuclii, O the oxygen nucleus. O is the centre of negative charge and of the molecule.

(a) Can be proved from the curve of X-ray diffraction of water, which is quite different from that calculated for an ideal liquid of the same density (see Fig. 2). It has also been shown that most of the physical properties of water, viscosity, compressibility, latent heat of evaporation, etc., cannot be explained on anv ideal liquid theory.

(b) From a knowledge of the spectrum and from the observed dipole moment of water vapour — and from that of hydroquinone in which the effect of a single -OH+

can be estimated—it is possible to find a charge distribution which indicates that water molecules must arrange themselves in a tetrahedral

co-ordination. Each molecule is surrounded by four others, as shown in Fig. 1, the binding being between the positive regions on one molecule to the negative on the next. Such tetrahedral co-ordination is found in ice.1 co-ordination Tetrahedral alone is, however, not sufficient to determine the structure completely. The polymorphous forms of  $SiO_2$ (cristobalite, tridymite, quartz), in all of which the SiO<sub>4</sub> groups are tetrahedrally co-ordinated, show some of the possible varieties. Now, ice is isomorphous with tridymite, and it seemed reasonable to guess that while water cannot be a disordered

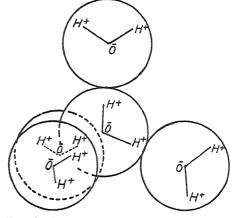
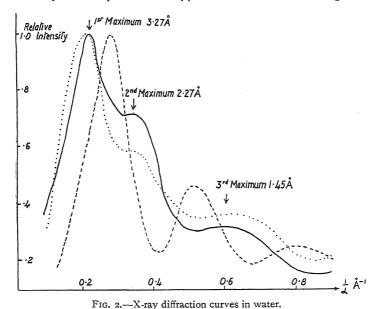


Fig. 1b.—Tetrahedral co-ordination of water molecules. The four molecules surrounding one water molecule are shown. Of these, two are in the plane of the paper and two above and below.

<sup>&</sup>lt;sup>1</sup> Barnes, *Proc. Roy. Soc.*, 125A, 670, 1929. Barnes' structure, which gave only oxygen positions, must be modified by a threefold multiplication of the cell and a change to a polar crystal class to explain both the molecular nature of ice and its trigonal symmetry.

ice structure—this could only give a decrease of density—it might easily be derived from the denser quartz structure. This structure would give the right density (using the value 1.38 Å derived from ice for the radius of the water molecule) and can be used as a basis for calculating the X-ray diffraction. If this is done, it can be seen from Fig. 2 that a very good fit is obtained which is improved by introducing a slight general disorder to account for heat motion. An ice-like structure gives a distinctly worse fit. However, it is noticeable that the X-ray diffraction curve of water tends at high temperatures to approach that of an ideal liquid, while at very low temperatures it approaches the ice-like arrangement.



Corrected experimental value (Amaldi).
Calculated value "quartz like" Water II.
Calculated value ideal close packed liquid Water III.

(On heating, the first maximum moves outward and the second inward, both approaching first maximum of Water III.)

From this follows the general picture of water as possessing an internal structure which can pass continuously through three stages:

Water I, Water II, Water III, ice "tridymite"-like, → "quartz"-like, → "Liquid ammonia "-like light, viscous. light, non-viscous.

Under ordinary pressures Water II predominates from 0° to 100° C., while Water I only occurs, and then not completely, in super-cooled water, and Water III only between, say, 150° C. and the critical point. There is no question of different molecules of I, II or III. The nature of water is determined by different geometrical arrangements of the same molecules in small regions of the liquid due to different amounts of molecular movement imposed by the temperature.

In each small region, containing a few hundreds to a few tens of molecules at different temperatures, the arrangement is pseudo-crystalline. These regions have an appreciable electric moment, and are needed to account for the large dielectric constant of water which is practically identical with that of crystalline ice for low frequencies. These cybotatic groups have a very small persistence in time, as is shown by the difference of the frequency relation of the dielectric constant of water and ice for which the times of relaxation are of the order of 10<sup>-12</sup> and 10<sup>-6</sup> seconds respectively.

These arguments can be used quantitatively to calculate the internal energy of ice and water from the water molecule model derived from spectra and dipole moments. Choosing the model represented in Fig. I, with an effective charge of + 0.5 electron at the H centres and - I electron at the centre of the sphere (this is displaced by 0.15 Å from the O nucleus), the heat of sublimation of ice at absolute zero is found to be II.5 Cal. per gm. mol., as against II.8 Cal. observed (the exact agreement is fortuitous). For water the calculation is much more uncertain, because heat motion cannot properly be taken into account. It is II  $\pm$  3 Cal. per gm. mol. at zero centigrade as against IO.7 Cal. observed, a value which is still of the right order. The assumption of an ideal liquid structure would give only a fifth of this value. In both cases the bulk of the internal energy is supplied by the electropolar attachments of neighbouring molecules.

The same model can be used to account for the nature of ionic solution. The mutual potential of an ion and water molecule can be calculated. from the known radius of the ion and of the water molecule and from this we can calculate the total heat of hydration of the ion. This is found to be of the form

$$U_h = \frac{\epsilon - \mathbf{I}}{2\epsilon} \, \frac{z^2 e^2}{R_{(r)}} \, + NP(r, z) \{ \mathbf{I} \, + f(r, z) \} - u_w,$$

where  $\epsilon$  is the dielectric constant, ze the charge of the ion, N its co-ordination number, P(r,z) the mutual potential of the ion and molecule depending only on its radius and charge for ions of the rare gas type (but having a constant additional value for 18 shell and coloured ions).  $R_{(z)}$  is the effective radius of influence of the ion inside of which the water is polarised, while outside of which the water can be treated as a normal dielectric, and f(r, z) is a small correcting term depending on Born repulsion forces. and on the polarisability and mutual effects of water molecules. Fortunately  $R_{(z)}$  and f(r, z) can be found empirically, for, as Fig. 3 shows, if the heats of solution of ions are plotted against their mutual potential P(r, z)with water, all the points fall on four straight lines for ions of charge-I, 2, 3, 4 electrons. In arriving at the absolute experimental heats of solution, use was made of the theory outlined above that the heat of solution was a function of the mutual potential, and the values for K+ and F-, for which the radii are approximately equal, were taken as nearly half the observed value for  $K^+ + F^-$ . The values for experimental and calculated ionic heats are given in Table I as well as the effective volume of the ion in solution. It will be observed that some ions have negative effective volumes. These can be shown to be permanently hydrated. They include all the positive ions, except the largest (K<sup>+</sup>), NH<sub>4</sub><sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Tl<sup>+</sup>, but only two negative ions OH<sup>-</sup> and (F<sup>-</sup>); K<sup>+</sup> and F- are doubtful cases. From the slope of the lines it can be seen that all univalent ions and Be++ are four-co-ordinated in solution, while all the others are six-co-ordinated. In the case of the polyvalent ions, far the greater part of the heat of hydration is derived from the attachment of this first layer. It is noticeable also in these cases that the heat of hydration approaches the total ionisation potential. This indicates that the effect of the ionising solvent is practically to replace a small charged sphere (the ion) by a much larger charged sphere (the ion complex) which has then a negligible electrostatic energy. The hydration or non-hydration of an ion has a profound influence on the state of the liquid. From this theory, and from a study of physical properties of ionic solutions, it can be shown that hydrated ions produce on the water an effect of tightening and regulating the structure exactly similar to that produced by lowering the temperature, while large unhydrated ions produce an increase of disorder corresponding to a rise of temperature. We may therefore consider ionic solution as producing a change in the "structural temperature" of water depending on the nature of the ions dissolved. This effect is most clearly seen in viscosity, where large ions actually decrease the viscosity in dilute solution. This concept

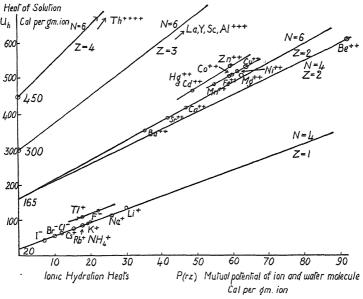


Fig. 3.

of structural temperature may prove to be very useful in biochemical and physiological problems where ionic phenomena are involved.

It is possible to go further on the basis of the theory to find the real nature of the H<sup>+</sup> ion in solution. The observed heat of solution of H<sup>+</sup> is 276 Cal. per gm. mol.; this is far greater than such an ion could normally have: we must account for it by an energy of formation of the hydroxonium ion  $(OH_3)^+$  of 144 Cal., plus 132 Cal. for heat of hydration of  $(OH_3)^+$ . The heat of hydration of  $(OH)^-$  is slightly less, 110 Cal. The most interesting fact, however, is that, if we calculate classically on the basis of the water models used, the energies in water of the ion complexes  $O_2H_5^+$  and  $O_2H_3^-$ 



TABLE	I.—PROPERTIES	OF HYDRATED	TONS

Ion.	Total Ionisation Energy.		n, Cal. per Gm.	Ionic Radius in	Effective Ionic Vol. in Solution
I Cal. per Gm. Ion.	Observed.	Calculated,	Å.	ca. Å.	
I+ .i+ .i+ .i+ .i+ .i+ .i+ .i+ .i+ .i+ .i	7070	276 136 114 87 80 87 97 655 57 47 608 489 410 376 346 1149 768 126 107 479 500 504 516 536 528 480 1185 980	130 116 92 87+ 79 85 130 105 95 655+ 57 49 600 495 408 376+ 346+ 149+ 980 830 768+ 1540+	0.00 0.78 0.98 1.33 1.49 1.65 1.35 1.35 1.35 1.35 1.35 1.36 1.36 1.36 1.36 1.36 1.36 1.36 1.36	- 8 95 5 + + 155 + 27 + 18 0 6 + 37 5 + 2 + 18 0 6 + 37 5 + 2 + 45 6 + 45 6 + 45 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6

are only slightly larger than those of H<sub>2</sub>O(H<sub>3</sub>O)<sup>+</sup> and H<sub>2</sub>O(OH)<sup>-</sup> respectively. In other words, the potential barrier for a proton moving from one water molecule to another is very small. This at once provides a theory for the abnormal mobilities of the  $H^+$  and  $(OH)^-$  ions. These do not only move bodily as other ions but also by a kind of relay race, as shown in Fig. 4.

Such a theory had already been put forward by Hückel, but with a very different mechanism for the actual transfer. The full theory involves a quantum mechanical consideration of the resonance between two equivalent states  $H_3O$ ,  $H_2O \rightleftharpoons H_2O$ ,  $H_3O$ , and the effect on this of an imposed electric field. This is, effectively, the hydrogen bond of Pauling. Apart from mobility, these account for most of the physical properties of acid and alkaline solutions. For example, the viscosity of concentrated H<sub>2</sub>SO<sub>4</sub> is due to three dimensional networks of hydrogen

<sup>\*</sup> Electron affinity.  $\dagger$  Used to fix R(z) and f(rz).  $\dagger$  Non-hydrated ions.

linked  $SO_4$  groups, an arrangement which is sterically impossible in the fluid  $HClO_4$ .

In conclusion, it is pointed out that a combination of our present knowledge of molecular structure with that of the mutual arrangements

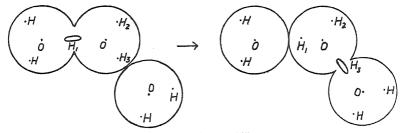


Fig. 4a.—H ion mobility.

H<sup>+</sup> moves effectively 1 atom  $\rightarrow$  when H<sub>3</sub> replaces H<sub>1</sub> as H bond ( $\bigcirc$ ) proton in  $(O_2H_5)^+$ .

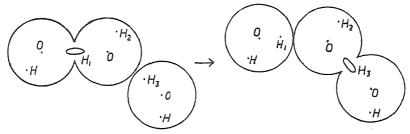


Fig. 4b.—(OH) ion mobility.

(OH) moves effectively r atom  $\rightarrow$  when H' $_3$  replaces H  $_1$  as H bond (  $\bigcirc$  ) proton in (O $_2$ H $_3$ ) .

of molecules in crystals seems now to offer a good basis for a quantitative attack on the general problem of the constitution of the liquid state.

## The Mobility of the Isotope Ion (H2)+.

Without insisting too closely on any of the details of the calculations here described but assuming merely that the model is approximately correct, we can show that the mobility of the isotope  $(H^2)^+$  must be much less than that of ordinary  $(H^1)^+$ . The only important effect of the change of mass will be to diminish very greatly the chance of jumping through the barrier from one water molecule to another. But the effect will probably be great enough to wipe out entirely the extra mobility of  $(H^2)^+$  or of  $(OH^2)^-$  due to the jumping and leave merely the normal mobility due to bodily transport of the  $(OH_3)^+$  or  $(OH^2)^-$  ions; mobilities probably not far different from those of  $(NH_4)^+$  or  $F^-$ . We may therefore conclude that the effective of  $(H^2)^+$  is about five times that of  $(H^1)^+$  and that of  $(OH^2)^-$  less than half that of  $(OH^1)^-$  in water.

This conclusion may be of importance in the separation of the isotopes of hydrogen by electrolysis of water, a separation which has already been carried almost to completion by G. N. Lewis in the University of California. It must not, however, yet be assumed that mobility is necessarily the dominant factor—here electrode processes will also discriminate (if at all) to favour the more rapid removal of H<sup>1</sup> from the solution and may be equally or more important.

If, however, the anomalous mobility of H1 is found effectively to have vanished with H2 we may, according to our theory, expect a perceptible difference in the physical properties of corresponding H1 and H2 compounds if, and only if, the H1 is one that could take part in a hydrogen bond that is chiefly in acids and alkalies. For example CH<sub>4</sub><sup>2</sup> would be apart from density indistinguishable from CH<sub>4</sub>1, but H<sub>2</sub>2SO<sub>4</sub> and NH<sub>4</sub>2OH2 would differ in physical properties from H<sub>2</sub>1SO<sub>4</sub> and NH<sub>4</sub><sup>1</sup>OH<sup>1</sup>. An attempt to test this was made with about I mg. of H<sub>2</sub>2SO<sub>4</sub> made from SO<sub>3</sub> and 93 per cent. H<sub>2</sub>2O prepared by G. N. Lewis. To determine its boiling-point the capillary tube containing the acid was put in the hot wire apparatus (described in the preceding paper, Bernal and Crowfoot), and the length of the bubble of vapour formed used as an indication of the boiling-point. No difference could be observed in this way between  $H_2^1SO_4$  and  $H_2^2SO_4$  indicating that their boiling-points cannot be different by more than 20° C. For better determinations and for their interpretation it will be necessary to wait until larger quantities are available.

#### FOCAL CONIC STRUCTURES.\*

By SIR WILLIAM BRAGG (London).

It may be convenient to set down the principal properties of a family of Dupin cyclide, as I am not aware of any easily accessible exposition.† Consider the ellipse,

$$\frac{X^2}{a^2} + \frac{Y^2}{b^2} = 1 : Z = 0.$$

Let (x', y', o) be a point on this ellipse, and k be a constant length. A cyclide of Dupin is the envelope of the series of spheres given by the equation:

$$(X - x')^2 + (Y - y')^2 + Z^2 = \left(\frac{cx'}{a} + k\right)^2$$
, where  $c^2 = a^2 - b^2$ .

The various members of a family of cyclides are obtained by giving different values of the constant k.

It is easily found that the equation of the envelope is

$$(X^2 + Y^2 + Z^2 + b^2 - k^2)^2 = 4(aX + ck)^2 + 4Y^2b^2.$$

\* In the course of his experimental demonstration of the apparatus described in his paper (page 915), Dr. van Iterson asked whether the phenomenon of the focal conics could be explained on the swarm theory. Sir William said that an explanation could certainly be given in terms of Friedel's hypothesis of the nature of the smectic state. According to Friedel, the molecules are arranged in sheets which are disposed like consecutive members of a family of Dupin's cyclides. Such a family is always related to two focal conics, and, again, according to Friedel, it is these pairs of conics that are the basis of what is observed.

This paper was communicated afterwards to amplify the explanation he

gave at the meeting.
† My attention has been called to a geometrical discussion of the Dupin Cyclide by Clerk Maxwell, Collected Researches II., 144.

The cyclide touches each of the spheres of which it is the envelope at all points of a circle, which lies in the plane

$$X - Y \frac{b^2 x'}{a^2 v'} + \frac{ck}{a} = 0.$$

Thus the cyclide has a set of circular sections, lying on planes which are parallel to the axis of Z, and pass through a fixed point on the axis of X.

Two members of the family of cyclides, depending respectively on the values k and  $k + \delta k$ , where  $\delta k$  is small, are at all points equidistant. This follows from the fact that the cyclide touches all its spheres, and a constant increase of  $\delta k$  in the radii of the spheres pushes the envelope outwards along the various radii by the amount of the radial increase.

Thus the Dupin cyclides satisfy the fundamental requirement that any neighbouring pair are equidistant at all points; in other words, they define surfaces of a form which can be assumed by a set of sheets of uniform thickness.

Consider now the conic

$$\frac{X^2}{c^2} - \frac{Z^2}{b^2} = \mathbf{I} : Y = 0$$
 where  $c^2 = a^2 - b^2$ .

This hyperbola, and the ellipse already considered, form a pair of focal conics. The vertex of each lies at the focus of the other. Also the hyperbola is the locus of the vertices of the cones of revolution of which the ellipse is a section, and *vice versa*.

The Dupin cyclide already found is also the envelope of the spheres

$$(X - x'')^2 + Y^2 + (Z - z'')^2 = \left(\frac{ax''}{c} + k\right)^2$$

where (x''Oz'') is a point on the hyperbola. The family of cycloids can be referred to the hyperbola just as well as to the ellipse.

It can be readily shown that the length of the line joining the point (x', y', O) to (x'', O, Z'') is

$$\frac{cx'}{a} - \frac{ax''}{c}$$

and is therefore equal to the difference of the radii of the two spheres centred at those points. These spheres, therefore, touch one another. Every sphere of the ellipse series, k = constant, touches every member of the hyperbola series given by the same value of k. The envelope touches both members of such a pair at their point of contact. Just as there is a set of circular sections of a cyclide all parallel to the axis of s, so also there is a second set all parallel to the axis of y.

A simple picture of the main features of these cyclides may be based on the consideration that every straight line which passes through both focal conics meets every member of the family of cyclides at right angles. In the special case when the ellipse becomes a circle, the hyperbola becomes the axis of Z. The cyclide are then "anchor rings" or "tores" to which every straight line passing through the axis of Z and the circle is obviously perpendicular.

Friedel's "focal domains" are generally the volumes included between two cones, the vertices of which are two points on the hyperbola, while the base is in each case the ellipse.

Within the domain the successive layers are bounded by cyclides. When the molecule is perpendicular to the layer the line joining any

point in one focal conic to any point on the other is parallel to the main axes of molecules all along its length: in other words, the optic axis at

every point lies on a line which passes through both conics.

Although, as we shall see, the physical explanation of the cyclide formation requires that little work is done in deforming any layer, yet this work must have a certain small value. Otherwise no layer would tend to straighten itself out. The energy due to the strain in any part must depend on the rate at which the optic axis changes its orientation measured along lines normal to that axis. The strain increases with the approach to the focal line: and may become exceedingly great. It is to this cause that Freidal ascribes the optical effects of the focal conics, and in particular the fact that they are visible.

The condition that two neighbouring members of a family of surfaces should be at all points separated by the same small distance can be satisfied by an infinite number of different families of surfaces, not alone by Dupin's cyclides. By what physical considerations may we account for the particular choice? A general explanation may, I think, be given

in the following way:-

As Friedel has pointed out, a layer formation in one part of a substance may not have the same orientation as a layer formation in another: and the focal domains may be considered to be regions of adjustment. We seek to know why the particular arrangement of the focal domains is chosen.

Certain conditions must be satisfied in the arrangement of the molecules in that portion of the medium where the adjustment is effected.

There is a strong tendency for the molecules to arrange themselves in layers. Every layer is of uniform thickness, which must be the length of the molecule, if the molecule is normal to the layer. There is also a tendency for each layer to arrange itself (by sideways movements) in respect to the layers on either side of it. If this latter tendency were completely satisfied the layers would become plane, and the ends of their molecules adjusted and held so that the layers resisted slipping over one another. The mass would become crystalline and the planes would probably become slip planes. But in the smectic state these latter tendencies are relatively small: the layers exercise very little shearing action on one another.

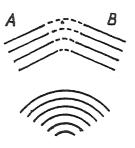
The energy in the layer, as in a soap bubble or surface layer in general, is proportional to the area: if the layer is stretched it becomes larger by taking in new molecules, the energy per unit area remaining the same.

If the layer is bent, the strain involves a certain amount of energy, but the layer stands much distortion as, for example, in the case of a soap film. A single layer floating in a mass of liquid which exerted no forces upon it except in the form of general pressure, would no doubt adopt a plane formation: several such layers lying parallel to one another side by side would tend still more to straighten themselves out, if they were not already plane, because of the forces tending to arrange the terminal atoms, and so to bring about the solid crystalline form.

If a set of sheets in one layer with respect to the terminal atoms in a neighbouring layer A has to be fitted to a set B, as in the figure, where the line of intersection is perpendicular to the plane of the paper, the substance in the space in which the adjustment occurs will tend to arrange itself in layers, as shown by the dotted lines; or, if a set of planes be in any way required to bend, the simplest form (and the

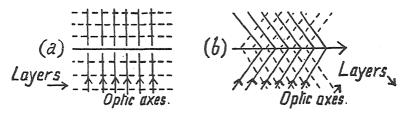
simplest form will always be assumed from energy considerations) is that in which the sheets are cylindrical. The nearer the axis of the

cylinder, the more intense the curvature and the greater the energy of the strain. A sufficient strain will have optical effects. The axis of this cylindrical bending may become visible as a line. It may be observed that a cylindrical bending must involve far less energy of strain than a bending into spherical sheets, which would result in a double measure of strain at the centre of the sphere. At such a point there would be a change of orientation in two dimensions, at a cylindrical axis in one only.



Thus a bending of a mass of sheets may, on the supposed conditions, take place in such a way that there is sufficient strain at the cylindrical axis to produce a visible line or thread in the medium. Such lines would bend and sway to and fro with the motion of the medium.

But a further step in the arrangement, based on such lines, is possible. It may be imagined that if the controlling circumstances demand it, the line already spoken of might be of not quite so simple a nature as the axis of a cylinder, complete or partial, but the locus of the vertices of a series of cones, or parts of cones. If, as an illustration of the point, we imagined a real thread running along the cylindrical axis as in (a), and supposed that we gave the thread a movement in the direction of its length, the cylindrical layers would become cones (b). The optic axes,



which are always perpendicular to the layers would become the generating lines of cones, whose vertices also lay on the thread. Such an arrangement, if produced in any way, would no doubt lead to further stress, because the strain is of less symmetry than the other, and would tend to disappear in favour of the simpler arrangement. Such an arrangement would be one of revolution about the line: again because the greater the symmetry the less the strain.

It is possible, however, to arrange the molecules and their layers so that their disposition is determined by two lines, not merely by one: and it is reasonable to suppose that an arrangement so determined is more stable than one in which the optic axes, while at one end they meet in a line, at the other are diffused in space.

This arrangement is that which has been outlined above in terms of the Dupin cyclides, and the two lines are the focal conics. It is the only arrangement in which the straight lines drawn from any point on either of two curves to all points on the other form a cone of revolution: and vice versa. All such straight lines are cut by the cyclides at right angles, and the cyclides are equally spaced. Thus the cyclides can define sheets of uniform thickness, and the form of the cones referred to is the simplest

possible, involving therefore the least energy of strain. Any attempt to rearrange the disposition of the sheets near the focal line or in intermediate position, or in other words to find different ways of arranging the terminals of the lines of the optic axes involves an expenditure of

energy.

Thus the "focal domain of Friedel" bounded by two cones of revolution of which the vertices are two points on the hyperbola, both of which pass through the ellipse, is an internally stable formation. Though as a whole it involves a certain amount of strain, the latter may be maintained by external forces, ultimately due to the form of the surface in contact with external bodies, and to any influences which such bodies exert.

# LIQUID CRYSTALS AND ANISOTROPIC MELTS.

#### A GENERAL DISCUSSION

Mr. Bernal (Cambridge) said: The theory of the forces giving rise to liquid crystals in section I. of Professor Oseen's Paper would seem to involve serious physical difficulties. If the force between molecules in a cholesteric liquid crystal depends on  $L_1 \times L_2$ .  $r_{12}$  so that it is not invariant for reflection in a plane then, as Professor Oseen points out, the laws of physics would have to be altered, or some quite unknown type of force invoked. It seems to me that this argument rests on a concealed error in the premises. By assuming in the first place that the molecules possess rotational symmetry he tacitly assumes that they possess internal symmetry of the second sort (i.e., planes or centres of symmetry). Now this is not the case for cholesteric molecules which are optically active and exist in enantiomorphic forms. Bearing this in mind the fact that for instance a system of right-handed molecules mutually arranged in a right-handed screw should have different energy from one where right-handed molecules are arranged in a left-handed screw is not only not surprising but physically necessary so that the necessity for invoking new principles disappears

In section 3 a very beautiful and elaborate theory is given for the behaviour of light in a spirally twisted medium. The question arises as to whether this theory which formally accounts for the best known properties of cholesteric substances is based upon a physically acceptable model. In particular the planes of Grandjean visible as fringes in a wedge-shaped preparation of an iridescent cholesteric substance are explained as an optical illusion. Before accepting this view it would be worth while to see whether the same phenomena could not be explained on the basis of some real physical periodicity of the order of 1000 to 10,000 Å. Friedel from exhaustive microscopic observations points to three main arguments in favour of the physical reality of Grandjean's

planes.

(I) The complex pattern of franges mobiles, virgules, etc., that appear between the Grandjean planes

(2) The nematic nature of the first Grandjean layer.

(3) The changing of the edges of the planes into nematic lines on "detorsion" by adding another cholesteric substance of opposite sign. The whole phenomenon strongly suggests schiller structure in minerals

and that due to regular twinning in potassium chlorate. The regularity may be due to "swarms" or "secondary structure" as in Zwicky's theory of solids. It would be very useful to find some critical experiment that could distinguish between these two apparently very different explanations of the same phenomena. The difficulty of finding such an experiment may however be an indication that here again as in the case of quantum physics we are trying to set up a fictitious difference between unobservables.

Dr. Lawrence (Cambridge) (communicated): Professor Oseen's remarks on the flow of ælotropic liquids cover what are at present two distinct problems; the flow of liquids containing anisodimensional molecules of normal size; and, secondly, the flow of those containing giant polymer-molecules or colloid micelles. Concerning the first, flow orientation requires very large rates of shear and departures from Newtonian flow have not been found. In the second class such departures are general, although confused in some cases by other phenomena such as elasticity. The factor determining the rate of shear required to orient any given particle depends, of course, upon its random kinetic motion. The distinction between the two problems is real insofar as anomalous flow requires, even for the most anisodimensional particles, molecular weights of at least 20,000; so that there is a big gap between them. In this discussion, the distinction is of peculiar interest since it makes Ostwald's demonstration of the anomalous flow of nematic melts evidence for Ornstein's Swarm theory.

**Professor Oseen,** in reply, wrote: The theory of the movements of anisotropic liquids is still in its infancy. The movements that lead to the forms of equilibrium of liquid crystals, cannot obey the law of Newton. Moreover, as to the theory of anisotropic liquids of small molecular weight, a theory of the motion is needed.

Professor Zocher (communicated): The energy and any other scalar quantity of a system cannot be changed, if the whole system is reflected at a plane. A change is only possible by a partial reflection, i.e., by reflection of the arrangement of the molecules without reflecting the molecules itself, if the molecules are not identical with their mirror images. Neither an ordinary vector nor an axial vector can represent the symmetry of a molecule of the cholesteric phase, only a combination of both representing the axis of symmetry of the molecule. Bearing this in mind, we find no difficulty in the assumption that the forces between the molecules are of an electrical nature. The magnetic moments of paramagnetic molecules cannot bring about orientation, because these magnetic moments are not attached to the molecules.

It is true that Oseen's theory does not yet explain all such observations as franges mobiles, virgules, etc., but it is not known what these observations indicate, and therefore it is scarcely possible to evaluate them as strong arguments against this theory. (At this point it may be emphasised that the supporting surfaces, e.g., mica, may be of great influence on such observations.) On the other hand, this theory explains several very important and striking phenomena, which are not explained by Grandjean and Friedel. I will mention only the following three facts for perpendicularly incident light:—

- (I) Only circularly polarised light of one sense of rotation is reflected.
- (2) The sign of rotation is inverted by reflection, for instance right-handed light is reflected as right-handed.
  - (3) Only one order of interference colours is observed.

I think, indeed, it is impossible to explain these facts, particularly fact (3), by assuming plans of discontinuity. (It is surprising that Oseen points out different orders for oblique light. The observations don't substantiate this.) Moreover, such interfaces in a homogeneous phase cannot correspond to the equilibrium, and at least thin layers without them should be observed. In Oseen's theory the spirally twisted system corresponds to the minimum of free energy. It is well known that addition of optically active substances causes a spiral twist in the nematic phases of p-azoxyanisol, etc. Why should it not happen that the period of twisting is equal to the wave-length of light? In that case the behaviour would be as described. According to Oseen's theory the perpendicularly reflected wave-length must lie between  $\lambda = 2pn_1$  and  $\lambda = 2pn_2$  (p being the physical period corresponding to a torsion by the angle  $\pi$ ,  $n_1$  and  $n_2$  the indices of refraction). In the proximate consideration which I gave in my contribution to P. P. Ewald's discussion in Z. Kristallographie in order to give a simple representation of the interferences in such a twisted system,  $\lambda$  is equal to 2pn. The analogy to the Schiller-structures seems to be evident, but the difference seems to be real and not only fictitious. Fact (3) may be considered as the needed experimentum crucis.

Professor Oseen (Uppsala), in reply, communicated: In two articles which have recently appeared, I have shown that there are phenomena in the iridescent strata which are accounted for in a simple way, if we regard the molecules as solid bodies without a rotatory symmetry around any axis. I am then of the same opinion as Mr. Bernal, that a complete theory must be founded on this general supposition. But even if we do this, the fact remains, that the phenomenologic theory leads to an expression for the energy, that contains terms which without new suppositions cannot be explained atomistically.

In the Discussion on Professor Freederickz' paper (page 919).

**Dr. Kast** (*Freiburg*) said: The orientation in electric fields is found in homogeneous electric fields, and when different concentrations of hydrochloric acid are added; it is only a function of the electric field

when the current density does not exceed 10<sup>-4</sup> amps./cm.<sup>2</sup>.

Professor Zocher (Prag) said: The existence of swarms of molecules with parallel dipoles seems to be most improbable, besides the other reasons against the swarm theory, since the dielectric constant of such a system must exhibit excessively high values which are never found in practice. The orientation in an electric field will be of the same kind as in a magnetic field, i.e., continuous deformation. If the experiments of Dr. Kast make it improbable that the orientation is caused by the anisotropy of conductivity, it may be possible that the orientation is caused by a convection movement in conjunction with the anisotropy of viscosity. The results of Fréedericksz seem to agree with this assumption.

Professor Ornstein referred to the linear character of the effect.

Mr. Bernal (Cambridge) said: This paper presents a wealth of important new experimental material. It is particularly valuable, not only for resourcefulness of the experimental technique—the method for examination of surfaces by differential total reflection is particularly valuable—but by the extension of measurements beyond the classical p-azoxyanisol to other liquid crystal substances. In particular, their work throws doubt on the simple dipole explanation of orientation in

the electric field. On the one hand, by the experiments on ethoxy benzal p-aminocinnamic ethyl esther in homogeneous fields, it appears that the longitudinal molecular dipole moment does not suffice to orient the preparation, even for 2000 volts per centimeter, while, on the other, acetoxybenzylazine, though symmetrical showed phenomena in all respects similar to those of polar molecules in inhomogeneous fields. These observations show us that the electrical orientation effects may have to be traced to complex electrostrictive or hydrodynamical causes.

The third part of paper on the mechanical elastic properties of liquid crystals opens up a new field in liquid crystal research, showing that, however fluid the liquid, directional distortion of the molecular axes is met by elastic resistance, even for such an extremely large period as I/300 sec. This certainty points to a mode of association not only greater than the molecular but greater than Ornstein's swarms, which have a relaxation time of IO<sup>-5</sup> secs.

Finally, the importance of this paper is that it goes far to redress the balance towards experiment in a subject of late heavily overloaded on the theoretical side.

Referring to Professor van Iterson's contribution (page 915).

Mr. Feachem (Cambridge) (communicated): Professor van Iterson showed a nematic liquid having in it two sorts of lines of discontinuity, broad and very fine streaks respectively. Lines such as these fine lines may be observed in the surface of the water of small rivers and streams, and more particularly when the stream is flowing fast and the motion clearly turbulent. In such a case the surface is ruffled with irregular undulations (not at all like wind ripples) and little vortices: among these the lines may be seen like very fine ridges on the surface. They wind about at random, and the characters of the undulations on either side of them are quite different: often they separate a smooth patch from a troubled one. Objects floating in the surface, and large waves, pass straight over them, but small ripples are refracted, and sometimes totally reflected by them.

Now in Professor van Iterson's demonstration, it is clear that there were temperature gradients in the specimen, and so there were probably small eddies, and if the lines observed on streams are due to the eddymotion of the water, it is surely reasonable to suggest that the lines in the nematic liquids are due to the same cause. If the lines observed on water are the intersections with the surface of boundaries between eddies, their similarity in appearance and behaviour to those in nematic liquids supports the suggestion that the latter are the boundaries between swarms. It would be very interesting to know whether the lines are also observed in specimens of nematic liquids in which temperature-gradients are carefully avoided.

In discussing Professor Vorländer's papers (page 899).

**Professor Ornstein** (*Utrecht*) said: It would be well to bear in mind the work of C. Hermann on the liquid crystal, which shows that there are many possibilities of orientation of molecules, to which different phases can be attributed. He thought that Professor Vorländer ought to recognise this work.

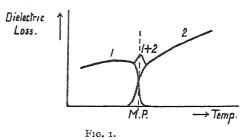
- Mr. Bernal (Cambridge) said: 1. Professor Vorländer's conception of mixed dimensionality is difficult to grasp in its mathematical aspect, but it plainly contains a physical principle of critical importance to the formation of liquid crystal phases. In this connection I should like to insist on the preponderating influence of spatial anisotropy of molecules. Optical, magnetic and even electrical anisotropy are far less important, because, for crystals that form anisotropic melts, the intermolecular forces are chiefly Van der Waals' attraction, the centres of which are spread pretty uniformly along the molecules. As regards the predominating influence of linear over planar forms it should be noticed that the aromatic ring is far less a plane structure than its chemical formula would suggest. If we allow a radius of action of 1.8Å. for the C-H groups derived from X-ray measurements, the benzene molecule appears as an oblate spheroid of polar semi-axis 2.2Å. and equatorial radius 3.2Å.; this is in marked contrast to its high optical and magnetic anisotropy. Under these circumstances it is not surprising that even simple para substituents lead to a molecule in which length rather than flatness is the predominating dimension.
- 2. The observed supracrystallinity of p-azoxybenzoic acid is in perfect accord with modern views as to the strength of the binding between carboxy groups due to the mobile H bond. The dicarboxylic acids, where the carboxyl groups are placed so as to be far enough apart and to be capable of linking together through hydrogen bonds in indefinitely long chains are particularly well crystallised and insoluble. A large number of organic substances supposed to be amorphous or polymerised undoubtedly must owe this appearance to extended hydrogen bonding.
- 3. In his remarks on the polymorphism of liquid crystals Professor Vorländer puts forward much evidence for the existence in certain cases of at least four intermediate stages between solid and isotropic liquid where Friedel maintains that only two (Nematic and Smectic) exist. I have examined some of the substances in question and am firmly convinced of the reality of the transformations observed (for details see the paper by Bernal and Crowfoot). I feel inclined to differ as to their interpretation. In every case the two highest temperature forms correspond to the classical description of Nematic and Smectic states. Whether the lower temperature forms, when they exist, are also liquid crystalline is more open to doubt, as here K. Herrmann's work shows that some lattice regularities exist and we may have to do with crystalline states admitting of molecular movement. I think the difference of these views is almost purely one of nomenclature and that, if this were recognised, most of the differences between the theses of Friedel and those of Vorländer would disappear.
- Dr. Kast, in presenting his paper jointly with Professor Ornstein said: With respect to the second maximum of dielectric loss, which we have observed at the melting-point (number 14 of the summary), I wish to give some further remarks. The extension of the measurements to further frequencies, and especially to lower temperatures, has shown that this phenomenon must be interpreted in another way. For, the loss-curve has a maximum in the solid state, which in case of lower temperatures normally shifts to lower frequencies. Owing to the fact that this leakage, in consequence of the variation of the friction-mechanism, ceases at the melting-point, while at the same time a new leakage arises through the conductivity, a depression of the loss-curve

takes place, which looks like a maximum (Fig. 1). Fig. 2 shows also that the curves observed at different frequencies agree exactly with this

conception. The different inclinations of the loss-curves for the liquid state is due to conductivity-loss in accordance with the formula

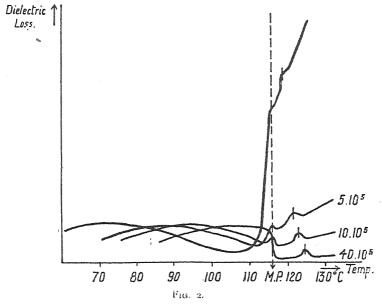
$$\omega$$
 .  $tg = \text{const.}$ 

Consequently, especially at the highest frequency, viz.,  $4\cdot10^6$  sec.  $^{-1}$ , the breaking up of the loss-curve of the



solid state becomes clear. Thus we have two loss-maxima for every frequency, one in the solid state, that is with great resistance to the movement and small particles, perhaps single dipoles, and the other in the crystalline-liquid state, that is with undoubtedly much smaller friction and consequently much larger particles, true molecule-swarms.

By reason of this new interpretation of the loss-curve, sections 14 to 15 of the summary must be omitted, and moreover the explanation of the conductivity-curve of Benzophenon cannot be maintained as a



result of a closer research. For, only by measurements with direct-current can a depression be observed in this curve, possibly because by reason of the temperature decrease arising at the melting-point there is a deficiency of ions. The considerations as to the conductivity of p-azoxyanisol and its increase by the orientation of the dipoles were, however, confirmed by very careful control. The measurements for this purpose were made at constant temperature whilst varying the electric tension. Moreover it was ascertained, by different additions of hydrochloric acid, that at current-densities under 10<sup>-4</sup> amp./cm.² we are

concerned with an orientation depending only on the strength of the dielectric field and affecting therefore, the dipoles themselves. Only when the current-density exceeds this limit, does the orientation become dependent on the density itself, as may be expected in the case of an orientation through the conductivity-anisotropy of the swarms or through a flowing of the melt. I have yet to point out, that in my X-ray-pictures the current-density always lies below this limit.

In the Discussion of this paper and that of Professor Zocher (page 945).

Professor Ornstein (Utrecht) said: One of the most striking properties of liquid crystals is their turbidity. It is necessary to give an explanation of this if we are to accept the idea that the liquid crystal forms an aggregate of homogeneous anisotropic regions. By reason of the double refraction the light is scattered. The effect of the clustering tendency shown clearly by liquid crystals is a quite general phenomenon (compare the Barkhausen effect in monocrystalline iron which shows the same phenomenon). Zocher, in his theory, neglects the action of Brownian disturbing forces, and his equation gives no better a description of the facts than Okuba's and Honda's non-static heat considerations of the theory of fero-magnetism. Professor Zocher said: As I showed in an earlier paper, we must distinguish between two kinds of turbidity. The first kind results from the Time deformations in the 40 bi-refringent um which are characterised by the well-known lines of discontinuity. The second kind is visible also in homogeneous regions of the nematic state, and is probably caused by a Brownian movement. This movement consists in small deviations of the elements of volume from their equilibrium positions. Only this second kind of turbidity, which does not exist in the smectic state should be treated by a kinetic theory similar to the swarm theory. **Dr. Kast** (*Freiburg*) then exhibited new curves as follows to explain the scattering of light: The hypothesis of swarms of parallel molecules does not exclude the possibility of larger homogeneous regions; rather, it explains their occurrence even when the external forces are very small. The turningmoments are large because they act not on single molecules, but on whole swarms. In particular, reference may again Fig. 3. be made to the occurrence of such uniform regions immediately in contact with the limiting surfaces of glass or metal.

The swarm theory, however, postulates an essential difference between the surface of the preparation and its interior. This is clearly shown by some new measurements on the scattering of light by layers of different thicknesses of p-azoxyanisole in the anistropic-liquid state, illuminated with sodium light. It is known that the transparency in the direction of the field is increased in the magnetically oriented state. We have recently recorded the disappearance of this increased transparency on

the removal of the iron-free magnetic field, using an apparatus with a small time-lag (a selenium-silver photo-element, used with a Moll galvanometer). In the diagram, the increase in transparency for a field of 1650 gauss was put equal to 100 for each bulb. It is clear that the type of recovery of the original transparency is completely different for the different thicknesses. In particular, it can be seen that up to a distance of more than I/100 mm. from the outside the increase disappears within I second (bulb 0·I mm.), and is succeeded by a large temporary increase in turbidity; whereas for thicker bulbs (0·5 and I mm.) it is some minutes before the increase in transparency has disappeared. This is in excellent agreement with our hypothesis that the preparation at the surface is affected by external forces which bring about parallel setting, while in the interior it is only the temperature fluctuations of direction that can eventually destroy the magnetic orientation.

**Professor Zocher** (*Prag*) said: The enormous difference between the layers of 0.5 and I mm. proves, that the influence of the walls reaches over a distance of at least several tenths of a millimetre. The same fact is well known from the optical observations of Mauguin, and seems to be incompatible with the statement of the swarm theory, that the diameter of one swarm is 10<sup>-5</sup> cm.

**Dr. Kast** (*Freiburg*) said: The structure of the parallel molecules is the determining point for their liquid crystalline character; clusters are found in many other cases, *i.e.*, isotropic liquids as well as solids. The significance of the melting phenomenon is the transition of one phase with one structure into another phase with another structure (see Nos. 16-17 of the Summary).

**Dr. N. K. Adam** (London) said: How sharply does Professor Ornstein think that the swarms are defined at their boundaries? In other words, how thick, approximately, is the transitional layer between one swarm and another, or the surrounding liquid? The phase boundary between a liquid and a gas is quite thin of the order, 10<sup>-7</sup> cm.; are these swarms to be considered as separate "phases"?

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Professor Ornstein (Utrecht), in reply, said: The swarms are differently oriented parts of the same phase. In the optical considerations on turbidity a sudden transition between the separate parts is postulated, and the calculations on this basis are in accordance with the facts. However, it is conceivable that transition layers exist which can be of larger dimensions that those between liquid and gaseous phase under normal circumstances, but are of the order of those which are present near the critical point where the clustering tendency as has been shown by Zernike and Ornstein, is of great importance.

Mr. Bernal (Cambridge) said: Professor Ornstein and Dr. Kast have collected in this paper a large number of results, both experimental and theoretical, and have shown that all of these are in accordance with their swarm hypothesis of liquid crystals. What they have not in my opinion succeeded in proving is that the existence of swarms follows necessarily from the observations or that another hypothesis might not as well account for the facts. Of the phenomena discussed some (the orienting effects of surfaces, the slow re-establishment of equilibrium on the removal of disturbing fields) find a common explanation in any theory which is based on a mutual tendency to parallelism between molecules. There remain two important arguments for the swarm theory, one based on Riwlin's measurements of extinction in nematic para-azoxyanisol, and Kast's measurements on the orientation of nematic p-azoxyanisol in

electrical fields. As to the first, the swarm theory here leads to the correct formula for the extinction varying as  $(d-0.04)(n_1-n_2)^2$  where d is the thickness and  $n_1$  and  $r_2$  the refractive indices. However, extinction would arise without swarms, merely from the continuous variation of direction of molecules from place to place. This must necessarily be a function of the birefringence, and would probably depend on the second power, as the size of the swarm does not, in Ornstein's theory, explicitly enter into the index. Similarly, on any theory the effective thickness of the layer would be bound to be less than the real thickness, because of the more perfect orientation near the walls. The agreement with theory is not, therefore, conclusive for the existence of swarms.

The evidence from electric orientation gives more definite information, but is not so simple to interpret. In the first place, it is unfortunate that so much elaborate physical measurement has been made on the classical liquid crystal *p*-azoxyanisol because its real chemical constitution is still in doubt and what is known of it is difficult to reconcile with the physical data. These are essentially that:—

(I) The dipole moment is  $2.3 \times 10^{-18}$ , measured in solution.

(2) For ordinary frequencies the dielectric constants are  $\epsilon_1 = 5.4$ ,  $\epsilon_2 = 5.5$ ,  $\epsilon_2 - \epsilon_1 = 0.1$ , where I and 2 refer to orientations with the molecular axes parallel and perpendicular to the electric field.

(3) In fields of low strength and relatively low frequency, the axis of

the molecule lies parallel to the field.

Combining (I) (2) and (3), Ornstein assumes that the dipole moment of the molecule lies along its long axis, but that the polarisibility of the molecule is greater perpendicular to the long axis.

The chemical formula of p-azoxyanisol can be written

$$CH_3$$
 $CH_3$ 
 $CH_3$ 

In (a), where the O atom is held by a semi-polar bond to one N atom, the dipole axis is highly inclined to the molecular axis; in (b) where the O atom is shared in some unspecifiable way with both N atoms, the dipole moment is perpendicular to the molecular axis. No way of formulating p-azoxyanisol has been suggested that will make the dipole moment lie along the molecular axis. If we are to reconcile this fact with the electrical observations, the most plausible assumption is that the molecules in the liquid crystal state are rotating. This is not unreasonable, as already in the crystal their benzene planes are nearly at right angles.

If we accept formula (a) this would give a component of the dipole moment along the rotation axis, and would also explain the larger

polarisibility at right angles to the axis where the effect of the perpendicular component of the dipole moment overcompensates the greater longitudinal polarisibility of the static molecule. This assumption would reduce the effective dipole moment of the molecule to  $1 \cdot 1 \times 10^{-18}$  e.s. or less, but otherwise would fit with Ornstein's assumptions. If the molecules do not rotate, on the other hand, it is quite plain that with either formula (a) or (b) the dipole moment does not orient the molecules, even for low fields and some other mechanism, streaming phenomena, electrostriction, etc., must be invoked.

This possibility is not to be excluded as the experiments Freedericksz and Zolina show. The first estimate of swarm size given by Ornstein and Kast is based on the existence of a swarm dipole moment  $p \gg 10^{-14}\,\mathrm{e.s.}$  But, apart from the uncertainties mentioned above, this swarm dipole moment may be considered as a simple measure of the directional coherence of neighbouring molecules whereby the electrical turning moments of external fields on individual molecules are compensated

over a far greater range than for normal liquids.

More significant are the extremely important experimental facts, brought out by Kast, that for fields of greater frequency than a certain critical value, the molecular axes set perpendicular instead of parallel to the lines of force and that, near this frequency, there is a considerable dielectric loss due to the reorientation. The order of magnitude of this critical frequency,  $10^5 \rightarrow 10^6$  per sec., shows conclusively that there is involved something of much greater magnitude than a simple molecular orientation. But the further investigation of the variation of critical frequency with temperature shows that the simple swarm theory is not adequate to account for the phenomena, for this frequency changes nearly a hundredfold within a temperature change of 6° C., while the size of the swarm decreases, at most, to a third. The knocking together and deformation of the swarm is not a happy hypothesis to explain this discrepancy, for if the swarms are so deformable as to be completely broken up in times of 10<sup>-6</sup> secs., much shorter than their presumed normal "life," why need they be postulated in the first place?

We may conclude that the best defence of the swarm theory would seem to be at present as follows. A somewhat discontinuous aggregation of molecules is to be expected in liquid crystals by analogy with similar textures occurring in other states of matter (i.e., Zwicky texture in solids, association swarms at the critical point, etc.). It is also a useful model for imagining the structure of a liquid crystal in bulk (as against its microscopical examination in thin layers). But up to the present we have neither theoretical knowledge to prove the necessity of swarms from the properties of molecules, nor the experimental observations to deduce it from the study of liquid crystals themselves.

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Finally, while agreeing with Professor Ornstein that the swarm theory has been an extremely fruitful working hypothesis, as is amply shown by his own work and that of his collaborators, it would be a grave mistake to assume further that any other theory such as the deformation theory of Zocker has not as much right to justify itself.

With regard to Professor Zocher's paper, I would like to call attention to the physical meaning of two of the constants,  $k_1$ ,  $k_2$ , referring to lengthwise or cross distortion between molecules. Zocher states that when

electrical fields. As to the first, the swarm theory here leads to the correct formula for the extinction varying as  $(d-0.04)(n_1-n_2)^2$  where d is the thickness and  $n_1$  and  $r_2$  the refractive indices. However, extinction would arise without swarms, merely from the continuous variation of direction of molecules from place to place. This must necessarily be a function of the birefringence, and would probably depend on the second power, as the size of the swarm does not, in Ornstein's theory, explicitly enter into the index. Similarly, on any theory the effective thickness of the layer would be bound to be less than the real thickness, because of the more perfect orientation near the walls. The agreement with theory is not, therefore, conclusive for the existence of swarms.

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More experimental work needs to be done, particularly with other substances than p-azoxyanisol, to separate the essential from the accidental influences of magnetic, electric and optical anisotropy.

Finally, while agreeing with Professor Ornstein that the swarm theory has been an extremely fruitful working hypothesis, as is amply shown by his own work and that of his collaborators, it would be a grave mistake to assume further that any other theory such as the deformation theory of Zocker has not as much right to justify itself.

With regard to Professor Zocher's paper, I would like to call attention to the physical meaning of two of the constants,  $k_1$ ,  $k_2$ , referring to lengthwise or cross distortion between molecules. Zocher states that when

 $k_1\gg k_2$  a smectic substance results with straight axial lines. This, it seems to me, is confusing cause and effect. The fundamental physical characteristic of smectic states is the existence of regularly spaced planes of molecules which is due to a minimum of potential energy when two molecules lie not only parallel but with ends aligned — rather than —. These planes can be distorted only into Dupin's cyclides, as Sir William Bragg has pointed out, the normals to which form a system of straight lines along which the molecules must lie, hence arises the straightness of the axial lines and the fact that  $k_1\gg k_2$ .

As regards the very interesting observations on orientation anomalies in nematic substances, it would seem that these are more apparent than real. Although for the greater number of substances the axes for greatest refractivity and susceptibility are the same, there is no theoretical reason why this should be the case. In molecular substances both are vectorially additive properties of homopolar bonds, but the constants for the bond types do not necessarily follow in the same order, and optical refractivities, as they depend on electrical deformability, are much more affected by ions and local dipoles in neighbouring molecules. The exceptional cases of potassium laurate and salvarsan are probably to be explained in this way. In the first case, the bi-refringence of aliphatic chains is small, and might be reversed by the action of water molecules or K<sup>+</sup> ions; in the second, effect of the arsenic atom must be large on the optical properties, but small on the shape of the molecule.

**Professor Zocher** (communicated) wrote: It seems that Dr. Bernal has not understood me, in consequence, possibly, of a mistake of translation. I wrote in my paper, that the behaviour of the smectic phases results from the fact, that  $k_1 \gg k_2$ . In general, it is possible to derive the mechanical properties of the phases from their molecular structure, i.e., that in the smectic phases  $k_1 \gg k_2$ , and from the mechanical properties we can derive the arrangement of the optical axis in a deformed region. This is what Oseen did, and Sir William Bragg's derivation can be considered from the same point of view.

I think also that there is no unconditional reason why the axes of greatest refractivity and susceptibility should be the same. What we wished to prove first was, whether the axis of symmetry is always the axis of greatest susceptibility. This might be expected, because the axis of symmetry is regarded as the length of the molecule, *i.e.*, the direction of the greatest number of chemical bonds. In another paper I examined whether the axis of symmetry is always that of the greatest refractivity. It could be shown, that the greater polarisibility (for light) of the length of the molecule can be overcompensated by the action of those parts of the molecule which have a stronger polarisibility perpendicularly to it. This negative component of double refraction may be due to ionisation, since it is magnified by heating or by addition of water. Salvarsan has only positive double refraction.

**Professor Desch** (*Teddington*) said: It would be interesting to know whether, when a mass of a substance in the liquid-crystalline state, sufficiently thick to eliminate the orienting effect of glass walls, is kept at a constant temperature for any length of time, any effect of the nature of "Sammelkristallisation," or grain growth, could be observed. On the supposition that the mass consists of swarms of oriented molecules, separated by regions with random orientation, it might be expected that a condition of greater stability would be reached when the small units had agglomerated to form larger ones. Such an effect might show itself

as a diminution in the turbidity with time. If the effect were not found to occur spontaneously, would it occur after more or less parallel orientation had been brought about by means of a magnetic field? A compari-

son with grain growth in metals suggested this question.

**Professor Zocher** (*Prag*) said: The recrystallisation of nematic and smectic substances must be quite different from that of crystalline phases, because there are no interfaces in which the substance can migrate from the small crystals to larger ones. A bending closed in upon itself, as in the conic structures in the smectic state, can only be resolved by a rupture. The activation energy for this rupture, in general, is probably too large to be available. In the nematic state we have the same case for the deformations along the lines of discontinuity. On the other hand, the elasticity of nematic phases (see my paper) is so small that external forces giving rise to new bending scarcely can be excluded. Even if we have made a uniform orientation by the aid of a magnetic field, deformations reappear after removal of the field. In freshly prepared layers with many deformations a transition into more homogeneous structure can be observed: some of the lines of discontinuity disappear by contraction.

**Professor Lowry** (Cambridge) said that he was very glad that Professor Iterson had mentioned the "confocal conics" which Friedel had observed in smectic media. The parallel orientation of molecules, which had formed the principal topic of discussion up to this point, was simple and easy to understand, but was less fundamental and important than the remarkable figures which were observed when this regular orientation was destroyed, and it would be of great interest if an explanation could be given of the arrangement of the molecules which gives rise to these figures.

Mr. Rawlins and Dr. Lawrence (communicated): The texture of the focal conic structure varies with the conditions and with the nature of the substance. It is clear that the form of any surface of a family will depend upon its value of k, but the actual shape observed is the particular member  $k_{\max}$  of the family, where  $k_{\max}$  is the value of k for the outermost surface. The texture under different conditions will also vary with the values of the constants a, b, c, and it scarcely seems likely that these will all have the same temperature coefficient: thus, any one substance may show a different texture at different temperatures.

For molecules of different shapes, the texture may vary: for small values of k, where the strain is greatest (as Sir William Bragg has pointed out, page 1058), molecular configuration may be expected to exert its greatest effect upon the packing; here the need for maintaining dk constant (as the geometry requires) results in the most marked differences of arrangement of molecules of different shapes. This effect must show itself in the relative values of a, b and c. These phenomena can be observed by the traces.

**Professor Herrmann** (Charlottenburg) said: With reference to the orientation of molecules of p-azoxyanisole in an electric field, found by Dr. Kast <sup>3</sup> as well as myself and my collaborators, <sup>4</sup> we now think it due to another cause. We attribute the orientation in a steady field to a secondary effect, the convection currents which are always present (loc. cit.). The critical frequency observed by Dr. Kast in an alternating field in which the angle is turned through 90° is explained by the same

<sup>&</sup>lt;sup>3</sup> W. Kast, Z. Physik, 71, 39, 1931, and also Z. Physik, 76, 19, 1932.

<sup>4</sup> K. Herrmann, A. H. Krummacher, and K. May, Z. Physik, 73, 419, 1933.

cause: The effect of the streaming particles disappears when the distance traversed by them during an alternation is comparable with the molecular length. This can be calculated numerically. The length is given by the expression:

$$l = \int_{0}^{\frac{\tau}{2}} uEdt = \int_{0}^{\frac{\tau}{2}} uE_{0} \sin \frac{2\pi t}{\tau} dt = \frac{uE_{0}\tau}{\pi} = \frac{uE_{\text{eff.}}}{.707\pi\nu}.$$

Here u is the "mobility" of the particle, *i.e.*, the distance traversed per second in a field of 1 volt per cm.,  $E_{\rm eff.}$  is the effective potential; u is almost the same for colloidal particles as for ions, on account of the much greater charge on the former; and the mobilities of the ions do not differ greatly among themselves. We put  $u=5\times 10^{-4}$  cm./volt. sec., which seems justifiable, since the viscosity of p-azoxyanisole is not much different from that of water. Using Herr Kast's figures,

$$E_{\rm eff.} = 650 \, {\rm volt/cm.}, \, \nu = 3 \times 10^5,$$

we obtain  $l=34.5\times 10^{-8}$  cm., a length which is comparable with that of the molecule of p-azoxyanisole.

We conclude that in the neighbourhood of these frequencies the convection currents lose their effect, and the molecules can no longer orient themselves in their natural positions in which the long axis is perpendicular to the lines of force, whether this is brought about by the direction of greatest polarisability (perpendicular to the long direction) or by the existence of a dipole moment. We consider that the more probable position of the dipole moment is perpendicular to the length, as this is more consistent with the structure of the molecule (even according to Angeli's formula). In this position, too, the molecule could follow the high frequency relatively more easily, because the moment of inertia is much smaller about the long axis than in a direction at right angles to it. However, this question could be decided by a measurement of the Kerr constant. Only if this had a negative value would Kast's explanation be possible.

Discussing Professor Foëx' contribution (page 958).

**Professor Ornstein** (*Utrecht*) suggested that it would be desirable if Professor Foëx would determine the permeability as a function of the magnetic field strength for given temperature in the liquid crystalline phase.

Mr. Bernal (Cambridge) said: Dr. Foëx' observations on magnetic susceptibility of p-azoxyanisol in the crystalline state confirm in a most satisfactory way the conclusions of X-ray analysis, his axis of greatest susceptibility coincides within two degrees with the direction found for the molecular length. As this is also the direction of largest refractivity a picture of the crystal as an assemblage of fairly close-packed rods is fully substantiated.

The comparison brought out between mesomorphous and magnetic phenomena is well substantiated, but it can only be a formal geometrical and not a physical analogy. As in the similar case of the "ferromagnetic" dielectric properties of rochelle salt which also show "Curie point" and Weiss law phenomena the common basis is the existence of a substance composed normally of regions each of which are anisotropic in some physical property. Usually the principal directions of each region are arranged in all directions, but by the application of suitable

forces they can be oriented in parallel. The attainment of parallelism will always be partially hindered by frictional forces and thermal agitation. In general, therefore, the induced orientation will only be possible for any such substance within a finite temperature range, below a certain temperature the rigidity will be too great, above another temperature the thermal agitation will prevent complete orientation however great the orienting force. Between these temperatures the whole range of phenomena of saturation and hysteresis will occur and the same laws will be followed with appropriate change of constants whether we are dealing with orientation of magnetic or electric moments or axial directions of neutral molecules. Similarly in every case the phenomena will be complicated by surface effects. I think it is important to state this formal analogy, so that the difference between the contributions of classical theory and quantum molecular theory should be kept clearly in view.

**Professor Foëx,** in reply (communicated): As Professor Ornstein has suggested, it would be interesting to study the susceptibility of the nematic phase as a function of the field at a constant temperature. I hope shortly to be able to take up this work.

The agreement noticed by Mr. Bernal between the results of magnetic and of X-ray study of the *p*-azoxyanisol crystal is particularly pleasing. It shows that, at least in certain cases, the measurement of the magnetic susceptibility can lead to conclusions relevant on the question of the orientation of molecules.

Mr. Bernal suggests that the analogy between nematic and ferromagnetic substances is purely formal, and has no physical significance. I quite agree. In the case of ferromagnetic substances the orientation takes place inside the atom (spin or electronic orbit). However this analogy was interesting to follow up, since it has already led to the discovery of two phenomena; the variation of diamagnetism with temperature and the very large and rapidly variable magnetic birefringence which exists around the clarification point.

# In discussing Professor Herrmann's paper (page 972):

**Professor Zocher** (*Prag*) said: Since the smectic phases of thallium soaps are optically uniaxial, it is improbable that the molecules are straight-tilted chains. I would believe that the chains are not quite straight, perhaps partly spirals so that their length standing parallel to the optical axis is shorter.

**Dr. Kast** (*Freiburg*) said: In the X-ray diagrams of the nematic phase the ring means the random orientation of the swarm axes (texture). The effect of the magnetic field is to bring about an orientation of the swarm axes.

Mr. Bernal (Cambridge) said: The point raised in this paper is of the greatest interest in its theoretical implications. It is very difficult to conceive how in a truly smectic substance molecules can exist inclined to the plane normals. In each plane of such a substance the molecules must be supposed to have every degree of freedom except perpendicular to the plane. Now if the molecules are inclined but haphazard in azimuth they cannot be close packed as they would be when normal and would comprise a much larger area in each layer in an arrangement very much like that of an expanded liquid monomolecular film.

It is difficult to imagine that such an arrangement would be stable,

besides this would imply a much larger change of volume on melting than is observed in thallium stearate. If we except the experimental proof of inclined molecules it therefore follows that the state cannot be truly smectic but must belong to one of the intermediate states already suggested by K. Herrmann in his other papers and treated theoretically by C. Hermann. In this case it would still remain to determine to which of these states thallium stearate belonged. Each layer with inclined molecules must be biaxial and the optical uniaxial character could only be due to the complete lack of azimuthal parallelism between planes.

An observation I have made since reading Dr. Herrmann's paper makes it still possible, though not likely, that the change from solid to liquid crystal is not so great as he has found. Thallium stearate is certainly smectic at 140° when the high temperature photographs are taken, but it crystallises in feebly biaxial plates (apparently rhombic) in which the optic axial angle changes continuously with the temperature in a way similar to that of gypsum. It becomes uniaxial a few degrees below the melting-point, then the axes cross and it becomes increasingly biaxial.

At about 100° there is an abrupt change and another form with smaller bi-refringences but the same orientation appears. This is the state stable at room temperatures and for which K. Herrmann found the spacing 42.05Å. Now the change in optical properties suggests forcibly that not only is there a change of slope of the chains in this high temperature form leading to a shorter spacing but that this change is reversed in the stability range of the high temperature form and that the chains are nearly perpendicular at the melting-point. It would be very interesting to check these observations by X-rays and thus find by direct measurement the slope angle in the smectic state.

Dr. Malkin (in presenting his paper, page 977), said: Professor Herrmann has recently published X-ray measurements which support in a striking manner the views advanced in my paper. Thus, ethyl azoxybenzoate, in the solid crystalline state, has a long spacing of 16·3Å., whereas in the liquid crystalline state, this increases to 20·25Å. Similarly, for allylphenetolazoxybenzoate, solid crystalline, 15·8Å.; liquid crystalline, 20·14Å.; ethyl phenylbenzalaminocinnamic acid, solid crystalline, 20·83Å.; liquid crystalline, 24·2Å.; corresponding in each case to tilted and vertical molecules respectively. Moreover, in addition to the increase in length of the long spacings, there is also a simplification of the side spacings in the liquid crystalline state, shown particularly in Figs. 4 and 5 of his paper.

Both these effects may be regarded as the direct consequences of rotation. The forces about the axis of rotation are radially symmetrical, and therefore any force tending to tilt the molecule is distributed evenly about this axis. The effect of rotation on the side spacings has been discussed by Müller, *loc. cit.* (1932 papers), in his original papers on rotation in the normal paraffins.

<sup>5</sup> Z. Krist., 81A, 317, 1932.

<sup>&</sup>lt;sup>6</sup> The case of diethylparaphenylene-bisaminocinnamate appears to require further investigation. There is a considerable discrepancy between the calculated length of the molecule given by Mr. Bernal (this discussion) and Professor Herrmann. The spacing of the solid crystalline form is also not easy to interpret, since it seems unlikely that an ethyl ester would crystallise in double molecules.

Professor Herrmann's results on the thallium salts show that in these cases the chains are tilted. An explanation of this unusually interesting case may probably be that owing to the size and powerful field of force round the thallium ion, only the hydrocarbon chain, and not the molecule as a whole is rotating. As a consequence, it is possible that thallium salts do not exhibit all the usual properties of liquid crystals.

It would be interesting to investigate the effect of weakening the field of force round the thallium atoms by means of alkyl groups, as for example in di-ethyl thallium stearate. Such compounds might be found to give liquid crystals with the molecules arranged vertically.

Dr. Adam (London) said: Rotation about the linkages between carbon and carbon in a chain may, if independent, give very complex cumulative effects like the lashing of a whip; this very probably occurs in the "expanded state" of monomolecular films spread on water. Is it not possible that something of the same effect may occur in the smectic state of liquid crystals? This would give the same effect, probably, on the "long spacing" revealed by X-ray diffraction as the simple tilt assumed by Professor Herrmann. If the molecules of thallium stearate were not simply tilted, but were undergoing the vibratory motions of the chain which probably occur in the "expanded" monomolecular films, while still remaining in their parallel layers characteristic of the smectic state, the symmetry might be that proper to a lower degree of orderly arrangement than a sheet of uniformly tilted molecules.

Mr. Bernal (Cambridge) said: I agree with Dr. Malkin that the alternations in properties of long chain derivatives are to be traced to the sterical arrangement of the end groups, but I cannot accept his suggested explanation as shown in his Fig. 1. There can be no question of end linking of chains through methyl hydrogen interlocking. The hydrogens of the terminal methyl are certainly, at all the temperatures considered, rotating about the last C—C link forming, therefore, a diffuse approximately spherical shell of radius about 1.8Å. and argon like properties. It is possible, however, that such a model might give the same results as Dr. Malkin's, but it would be premature to attempt to calculate them until we are more certain of the position of the carbon atoms.

**Dr. Malkin,** in reply, said: The diagram (Fig. 1a) is not intended to suggest any rigid interlocking, but is given merely to indicate how the potential of the system may be higher, owing to the closer proximity of the protons of the terminal hydrogens and the electrons surrounding the terminal, or even penultimate carbon atom of the opposite chain. In case b, Fig. 1, I quite agree with Mr. Bernal that the terminal groups are rotating, but in case a, I consider the rotation somewhat restricted, and not inconceivably, sterically limited to extreme oscillations.

Unless the possibility of restricted rotation is accepted it is very difficult to explain certain well-known melting-point phenomena, namely, the higher melting-points of many branch chain isomers. A well-known case is that of normal butyl alcohol CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (M.P. — 80°) and its isomer tri-methyl carbinol (CH<sub>3</sub>)<sub>3</sub>C. OH (M.P. + 25°). Accepting Mr. Bernal's suggestion, the associated molecule of the latter would be regarded as a pair of hydroxyl groups surrounded by diffuse argon like shell of six methyl groups, a view hardly compatible with the relatively high cohesion suggested by the melting-point difference. If, however, the molecules are so far removed from each other that there can be no

<sup>&</sup>lt;sup>7</sup> Dr. R. C. Menzies and I are investigating a series of these compounds.

steric restriction, as for example, in the liquid state, Mr. Bernal's views are probably correct. This is reflected in the lower boiling-point of iso, and tertiary compound as compared with normal isomers.

With reference to Professor Stewart's paper (page 982):

**Dr. Kast** (*Freiburg*) said that the nematic swarm might be expected to have another structure such as the cybotactic; they are not merely

enlarged cybotactic swarms.

**Professor Ornstein** (*Utrecht*) said: The difference between these swarm types is that the one can be orientated by external fields whilst the other cannot. He laid emphasis on the large moments operating on the swarms as such which are essential for the cluster theory. The moment of a single molecule is not sufficiently strong, but that of a group of orientated molecules in swarms is much larger. The swarms in cybotactic texture are so arranged that only a few molecular moments are unsaturated by those of other molecules. It would be essential to make measurements of the range of intensity in the rings, which ought to be different for cybotactic and nematic swarms.

Mr. Bernal (Cambridge) said: It is extremely difficult, in fact it seems to me theoretically impossible, to account for the disposition of matter in an amorphous body: glassy, liquid or gaseous-solely on the basis of X-ray diffraction curves. The theory of crystalline X-ray diffraction shows that in order to deduce rigorously the electronic density at point in a cell it is necessary not only to know the intensity of the diffracted radiation but also the phase, and this can never be determined experimentally. This leads to a triply infinite ambiguity even in the most symmetrical case. For liquids to this ambiguity is added another in that we have no way of distinguishing an X-ray pattern due to a homogeneous liquid from that of a heterogeneous one. At each angle we observe a certain intensity of diffraction, but whether this is derived from one or more different internal patterns of molecules we have no way of telling. In building, therefore, as Professor Stewart has done, a picture of the structure of liquids on the basis of X-ray diffraction some criterion other than X-rays must be used to distinguish between different arrangements, all of which would give the same X-ray pattern. This criterion must be sought in a knowledge of the nature of the forces between molecules in a liquid. Now Professor Stewart has expressed the structure of liquids in terms of cybotactic groups, but it is very difficult to get an adequate verbal or mathematical conception of such a group. Two extreme definitions might be given, in the first a cybotactic group is conceived of as a microcrystal of 10-100 molecules and the liquid is imagined to be composed of such groups and free molecules. On the other extreme the cybotactic group is a mere way of expressing the fact that in any small volume of the order of 10<sup>-16</sup> cm, the molecular orientation and the distance between neighbouring molecules does not vary appreciably. In this view no distinction is drawn between one part of the liquid and another, and there are no free molecules. Professor Stewart would lean to the first view. I personally prefer the second as involving less assumptions. It should be emphasised that these two very different pictures would give identical X-ray patterns as would any intermediate picture.

To prove the existence of cybotactic groups would require evidence other than X-rays, and such evidence is not yet forthcoming. It is

nevertheless quite justifiable to speak of a cybotactic *state*, if by this is only implied that the molecules in the liquid have not a completely haphazard arrangement.

The apparent similarity of the X-ray patterns of nematic and normal liquids is to be expected. X-ray patterns depend primarily on mean distances between molecules, while nematic properties depend on orientation. There is no necessary connection between the two. The explanation offered by Stewart is unjustifiably concrete. All that can be proved is that the regularity of orientation extends over a volume of much greater order of magnitude than does the regularity of intermolecular distance. The expressions "companies" and "regiments" are useful perhaps in visualising the liquid structure but dangerous in that they may be taken literally.

Professor Herrmann (Charlottenburg) said: It follows from the last paragraphs of Professor Stewart's paper, that the molecular arrangements which he assumes to occur in cybotactic groups are the same as those postulated for liquid crystals (e.g. by Friedel). The difference must be simply in the size of the groups. That such an increase in the size of the groups should occur with the suddenness of a change of phase, as it must do in the transition from amorphous liquid to liquid crystals, seems to me a very unlikely assumption.

Professor Porter (London) (communicated): Professor G. W. Stewart, in his paper, shows very clearly that certain X-ray maxima (in the case of ethyl ether) only appear when the volume is less than the critical value (whatever the pressure and temperature may be) and he appears to claim that an ordinate through the critical volume marks the dividing line between the liquid and gaseous states. I wish to point out that in doing this he is purloining a term which has a long-accepted meaning which it is still necessary to retain in its old sense, and is applying it instead as a criterion of the presence of "cybotactic groups." I wish to protest against this act of petty larceny. It is surely unnecessary to disturb the established usage (which is so important for the engineer) merely for lack of inventiveness in connection with the new phenomena.

# Professor Stewart, in reply, (communicated):

One cannot have too clearly in mind that X-ray diffraction from either crystals or liquids gives a statistical result and that the proof of the uniqueness of the "structure" in the liquid case is quite impossible. But the X-ray diffraction experiments of liquids are unmistakably giving some reliable information, showing the effect of not merely the lack of randomicity produced by volume, but the effect of molecular forces as well, and this is gradually altering our conception of a liquid. Naturally too much emphasis must not be placed upon any picture, yet one must have a working description, since this will be of assistance in any approach to an understanding of the nature of the liquid state. But it is hardly possible to select perfect words. A cybotactic "group" may seem to imply the existence of a definite boundary of a semi-orderly assembly of molecules, but of course there is no such boundary. At any instant there is a gradation from the most orderly portion to regions about not at all so orderly. The very fluid condition of the entire region precludes definite boundaries and the word "group" in such a connection would naturally not be concerned with boundaries. The words "cybotactic group" are thus not misleading.

Certainly it is highly desirable to demonstrate the cybotactic condition other than by means of X-rays. Perhaps even then we could not regard the case as actually proved. But the positive evidence from X-ray studies is not the sole basis of confidence in the existence of the cybotactic condition in liquids. Electron diffraction in thin oil films by L. R. Maxwell,\* shows with phytol and pump oil the same three rings as shown with X-rays, using pentadecane and tetradecane, although the wave-length with the X-rays is approximately ten times as great. This shows that a large change in wave-length does not bring to light a possible error in interpretation, and is thus additional favourable evidence. We know in addition that this concept is in harmony with general considerations, which certainly show liquids to be more like solids than gasses. Also there seem to be no experiments which raise a reasonable objection to the cybotactic view. This situation naturally leads one to accept the view as a working hypothesis.

The author is glad that Professor Porter carefully states that "he (the author) appears to claim." For, as a matter of fact, the author does not make the claim. He has no desire to alter the definition of "Liquid." There seem to be two definitions now in the literature and a third would only make matters worse. The author's sole interest at present is in what happens internally when the material is subjected to various conditions of pressure, volume and temperature. Moreover, the text makes clear that the critical volume could not be a dividing line, for the cybotactic condition must depend partly upon temperature. When our information is adequate, doubtless then additional terms may be proposed to describe the internal condition in the process of "liquefaction." Professor Porter's comment is an advance warning of protest.

# In discussion of Dr. Müller's contribution (page 990):

Professor G. W. Stewart (Iowa) (communicated): In proposing a cybotactic condition in liquids, it was not stated that there are small "crystal aggregates of definite spacings." Quite on the contrary, the groups are thought to be not perfectly regular at any point, not to have defined boundaries, and doubtless to differ from one another in the mean distance of separation of the molecules in any "spacing." Moreover, imposed upon this is the mobility, for the constituents of any group are not permanent. Bragg's law is not strictly applicable, and its use is only as an approximation. The peak in the X-ray diffraction intensity curve in a liquid indicates approximately the most probable "spacing." The interpretation of the 4.64 Å.u. in normal paraffins as made by the writer was not regarded as a conclusion, but rather as evidence of the consistency of the cybotactic view with known facts. The interest of the discussion was not in the value of the "spacing" for liquid normal paraffins, but in the general correctness of the cybotactic view. As the experiments with X-ray diffraction in liquids accumulate, it becomes more and more evident that the cybotactic view is quite essential. The groupings found are, of course, dependent upon a limitation of the value of nearest approach, and also upon the shape of the molecules, but these two are but aspects of the result of molecular forces which are directly responsible for crystalline structure and for cybotactic liquid groups. It

<sup>\*</sup> Phys. Rev., 44, p. 73, 1933. Similar experiments by Lark-Horovitz and Miller are not yet in print.

may be of interest to report that recently 8 electron diffraction in thin mineral oil films has been shown to give diffraction angle intensity peaks corresponding approximately to the distances reported by the writer, using X-rays in pentadecane and tetradecane, 4.64, 2.1 and 1.2 Å.u.

Mr. Bernal (Cambridge) said: I entirely concur with Dr. Müller's observations on the interpretation of the intermolecular halo in liquid hydrocarbons. It is impossible from X-ray data alone to determine the precise spacial relations of the chain axes, in particular whether they are in hexagonal or square array. To understand this, we must consider rather the a priori probabilities of such arrangements. Now carbon chains in the liquid are always rotating, and must be considered as cylinders exerting a non-directed van der Waals' attraction. This will result in a tendency to parallel lateral packing, but it will not, in general, lead to close packing of the carbon chains. Such close packing of carbon chains exists in the solid near the melting-point, as Dr. Müller has shown. A looser degree of packing without any necessity of even local regularity but still preserving a closest approach of 4.8Å. between molecules will necessarily lead to a shift in the diffraction maximum from its close packed value to larger values, 4.64Å, and beyond. At still higher temperatures, near the boiling-point, this picture would be altered by the break up of local parallel orientation by the bending of the chains, but that this does not occur near the melting-point is shown by the very existence of the 4.6Å. maximum, and by a density much higher than could exist for a tangle of crooked carbon chains.

**Professor A. M. Taylor** (Rochester, N.Y.), (communicated): We have recently found <sup>9</sup> that at an interface between glass and long chain fatty acids in the liquid state there is evidence of a doubly refracting layer which exists for a temperature range of a few degrees above the solidification point. This indicates orientation of the molecules even in the liquid.

Professor Zocher said: As to the swarm theory, it is impossible to find out the diameter of the swarm. Professor Ornstein calculates from experiments in a magnetic field the volume of a single swarm to 10<sup>-15</sup> cm. or the diameter thereof to 10<sup>-5</sup> cm. An aggregate of swarms of this size orientated at random gives no double refraction as a whole. On the other hand, from measurements of turbidity he calculates to 10<sup>-3</sup> cm. the thickness of a layer influenced by a surface. It is in fact possible to get homogeneous layers of the thickness of 2·10<sup>-2</sup> cm., and therefore the thickness of a single swarm should be of the same size. It is evident that such large swarms cannot exhibit Brownian movements, which will cause distribution at random.

According to Professor Ornstein's opinion, it is not necessary that the substance should be broken up into swarms, and it seems the experiments show that the nematic phases do not break up into swarms. To the smectic phases the swarm theory cannot be applied because a magnetic field has no effect on them under analogous circumstances.

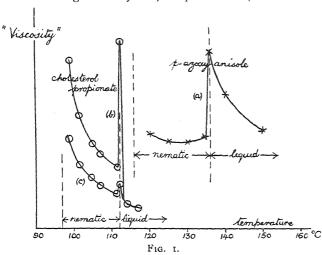
Therefore I think that consideration of the Brownian movement, which is the main content of the swarm theory, cannot be used for the explanation of the essential properties of mesophases. It finds application only to the before-mentioned turbidity of the second kind, *i.e.*, the turbidity of homogeneous regions in nematic phases.

<sup>&</sup>lt;sup>8</sup> These experiments were reported simultaneously by L. R. Maxwell and by Dr. Lark-Horovitz and E. P. Miller at the April, 1933, meeting of the American Physical Society.

<sup>9</sup> Taylor and King, *Nature*, 1933, 132, 64, and *J.O.S.A.* in press.

In discussing Professor Ostwald's paper (page 1002):

Dr. Lawrence (Cambridge) said: One of the criteria of nematic melts is high fluidity but, in spite of this, few measurements have been



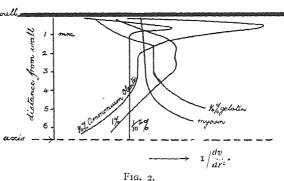
made of its variation with temperature the whole nematic range. In 1008 Schenck. working with p - azoxyanisole p-azoxyphenetole, obtained curves of the type shown  $(a)^{10}$ in Fig. 1 Recently Vörlander has found similar curves for the ethyl ester of cholesterol carbonic acid and

for some fatty acid esters of cholesterol. 11

Professor Ostwald has drawn attention to the fact that segregating mixtures show this peak in the viscosity curve and concludes that it is due to similarity of state of dispersion of the two systems. This comparison is misleading; the peak is not characteristic of the nematic melt at all, since it occurs at the temperature of transition, nematic to liquid. Since, in his examples, no indication is given of the transition temperatures from which the true state of affairs could be deduced, I have redrawn some of the results. In Fig. 1, curve (a) is for azoxyanisole, while (b) and (c) are calculated from Ostwald's Fig. 4 for cholesterol propionate. It is clear that the peak is not characteristic of the nematic melt, but that the viscosity of the latter is smaller than would be expected from the slope of the curve for the liquid substance.

The two curves (b) and (c) are for different pressures and rates of

flow, (c) being the higher where flow approaching Newtonian. seems, therefore, that the peak is only an indication that fictitivalues ous are being obtained for the viscosity that point, probably owing to turbulence.



<sup>Bingham, Fluidity and Plasticity, p. 209.
This vol., p. 899. Z. Krist., 79, 78, 1931; Berl, Isler and Lange, Z. Angew</sup> Chem., 37, 128, 1924.

The name "anomalous viscosity" is misleading in so far as it suggests a common origin to all deviations from Newtonian flow. Professor Ostwald's results for cholesterol propionate show clearly that there is anomalous flow in the nematic range, and an entirely different anomaly corresponding to the "peak" viscosity. Also, by a curious chance, in comparing nematic melts with sols of gelatin and of rubber, he is choosing three systems which show different types of anomaly.

It is often stated of anomalous viscosity that it varies with the rate of shear; but this adds nothing to our knowledge, since it is the rate of change of rate of shear that is the real unknown. In Newtonian flow (through a tube), the distribution of linear velocity across the flowing liquid is parabolic. In anomalous flow it is not; so I have observed directly the velocity distribution in several colloidal systems, examples of which are given in my paper in this volume (p. 1008). The general result is that the velocity is unexpectedly high at the wall and disproportionately low at the centre of the tube. From these curves the rate of change of velocity with square of distance from the axis,  $dv/dr^2$ , can be obtained. In a normal liquid, the reciprocal of this is the coefficient of viscosity multiplied by a numerical factor. This plotted against the distance from the wall of the tube would therefore give a straight line, but colloidal systems give curves which are characteristic of their nature. These curves may be regarded as the distribution of resistance to flow across the tube. Sols of the gelating type, such as gelatin, show marked increase of resistance to flow towards the axis whereas those of the type of ammonium oleate show a definite decrease. This latter type is anomalous, owing to the presence of large thread-shaped micelles. It is suggested that nematic melts are of this type.

Of Professor Oswald's three examples, the anomaly of nematic melts, whether or not it is due to anisodimensional aggregates of large size, is certainly different from that of the gelatin sol. Rubber sols, the third example, are distinct in another way. The solute is also present as anisodimensional particles, probably of a helical form, to which is due the characteristic elasticity of these sols, but each is a single giant molecule, whereas in the ammonium oleate type and the nematic melt the aggregate is built up from molecules of conventional size. These aggregates are therefore liable to degradation by shearing or by heating the system. Both of these factors determine the shape of the curves in Fig. 4.

It is clear that a complete analysis of the anomalous flow of nematic melts should yield valuable information concerning their constitution, particularly in connection with the swarm theory.

Professor Ostwald (communicated): Dr. Lawrence considers the comparison between segregation curves and viscosity-temperature curves of mesomorphic melts as "misleading" because the "peak" of the second-named curve "is not characteristic of the nematic melt at all, since it occurs at the transition nematic to liquid." Apart from the fact that a transition point belongs as a characteristic to both territories involved, I would like to point out that I have not compared "peaks" but "curves." The general form of the curves discussed is unquestionably the same. Furthermore, we naturally did not make measurements on the "peak" but on the "slopes" of the curve, including and preferring the nematic slope. As to the exact starting points on the slopes for our measurements, readers will find full account in a recent paper containing not only curves but figures (Koll.-Z., 63, 192, 1933).

I have never held nor expressed the opinion that "anomalous

viscosity" of different sols has one common origin. Just the contrary. I believe I was the first to point out in 1925—in opposition to certain views of H. Freundlich—that "already a priori half a dozen or more mechanical variables are to be expected" to account for the various experimental deviations from Newtonian flow (Koll.-Z., 36, 100). In a recent paper (ibid., 63, 76, 1933) on the anomalous flow of critical mixtures, I emphasise the fact that the word "structural viscosity" is a "Sammelbegriff" which denotes very different hydrodynamical phenomena, of which the anomalous flow of critical mixtures seems to represent a case of especially clear and relatively simple hydrodynamical conditions.

**Professor Ornstein** (*Utrecht*) said: The internal friction in a liquid crystalline liquid could be considered as the swelling of the swarms with deformation. It would be very interesting to study the double refraction and the turbidity of a moving liquid crystalline substance.

Referring to the late Geheimrat Rinne's Report (page 1016):

Mr. Bernal (Cambridge) said: I should like to say a few words of appreciation of this last paper of a great crystallographer. It is not given to many men at an age when most are content to rest on their laurels to open up a fresh field of scientific research, and to assess its importance with an intuition ahead of that of far younger men.

Rinne was not the first to see that liquid crystals had a bearing on biological problems, but I think he had glimpsed at the fundamental rôle that they played, and understood the essential nature of the pro-

perties that enabled them to do so.

The biologically important liquid crystals are plainly two or more component systems. At least one must be a substance tending to paracrystallinity and another will in general be water. This variable permeability of liquid crystals enables them to be as effective for chemical reactions as true liquids or gels as against the relative impenetrability of solid crystals. On the other hand, liquid crystals possess internal structure lacking in liquids, and directional properties not found in gels. These two properties have far-reaching consequences. In the first place, a liquid crystal in a cell through its own structure becomes a proto organ for mechanical or electrical activity, and when associated in specialised cells in higher animals gives rise to true organs, such as muscle and nerve. Secondly, and probably more fundamentally, the oriented molecules in liquid crystals furnish an ideal medium for catalytic action, particularly of the complex type needed to account for growth and reproduction. Lastly, a liquid crystal has the possibility of its own structure, singular lines, rods and cones, etc. Such structures belong to the liquid crystal as a unit and not to its molecules which may be replaced by others without destroying them, and they persist in spite of the complete fluidity of the substance. These are just the properties to be required for a degree of organisation between that of the continuous substance, liquid or crystalline solid and even the simplest living cell.

With regard to the contribution of Mr. Bernal and Miss Crowfoot (page 1032):

**Professor Ornstein** (*Utrecht*) said: The effect of the wall of one group of molecules is propagated through the liquid crystal to a depth of the order of a swarm, *i.e.*, about 0.01 mm. The experiments of v. Wvk

show that the layers at the wall also orient one another—interaction of swarms. The fact that there are swarms implies that on large complexes of molecules more force is exerted by the field. The experiments of the late Miss Riwlin show that a liquid crystalline aggregate consists of homogeneous layers of fixed double refraction. The extinction can be calculated as a function of  $d\omega^2$ ,  $\omega$  being the numerical value of the double refraction, d the thickness of the layer. The extinction of all nematic substances can be described by one formula which applies to all thicknesses of the preparation, and all wave-lengths. There can be no doubt that the swarm theory is a heuristic working hypothesis which has brought to our knowledge a great number of facts without requiring any new and special hypotheses. The chief problem now is to show from the molecular theory the necessity of the existence of swarms, in other words, to find from the molecular image forces of interaction between the molecules, which, together with heat motions, determine the mean cluster or swarm radius.

Mr. Carpenter (Southampton) (communicated): As the liquid crystalline condition is intermediate between that of crystalline solids and that of true isotropic liquids, it may be of value to review the state of affairs which obtains in a pure element at temperatures immediately above and below its melting-point, especially with regard to the question of sharpness of melting. The following are some of the relevant facts:—

I. In a single crystal there is no measurable self-diffusion, even at temperatures only a degree or two below the melting-point. poly-crystalline material the quite measurable solid diffusion, which increases rapidly with temperature, takes place at the boundaries between the crystal grains. 12

2. Macroscopically any way, the solid lattice collapses quite sharply at a melting temperature, which in general is known to be definite and reproducible within at least 1/10° C.

3. The change of electrical resistance of metallic elements on melting is sharp and discontinuous.<sup>13</sup> According to Bidwell,<sup>14</sup> the alkali metals are, however, an exception.

4. In the two cases (Pb15, Hg16) in which the true specific heat of an element of really high purity has been measured right up to the meltingpoint, no abnormal rise (rapidly increasing on approaching the meltingpoint) has been observed. The effect recently observed <sup>17</sup> in the case of Bi can be quantitatively accounted for by the amount of impurity (0.01 per cent.) known to have been present.

With regard to points (1) and (2):—

In order that an atom should change its place in a single crystal lattice, it would be necessary not only that it should possess a large amount of energy, but also that a neighbouring place in the lattice, to which it may move, should be available.

Thus, if atom A is to go over to the position previously occupied by its neighbour B, B must be capable of moving out of the way in order to create a vacant space for A. Since A and B cannot move through one another, B must be able to leave its normal position for another position

 <sup>12</sup> Hevesy, Nature, 115, 674, 1925.
 13 E.g., Northrup, J. Frank. Inst., 177, 1 and 287, 1914; 178, 85, 1914;
 Schulze, Z. tech. Physik., 11, 16, 1930.
 14 Physic. Rev., 23, 357, 1924.
 15 Klinkhardt, Ann. Physik, 84, 167, 1927.

<sup>&</sup>lt;sup>16</sup> Carpenter and Stoodley, Phil. Mag., 10, 249, 1930.

<sup>&</sup>lt;sup>17</sup> Carpenter and Harle, Proc. Roy. Soc., A., 136, 243, 1932.

other than that about to be vacated by A. Thus B also must possess more than the average energy, and the conditions in the neighbourhood must be such that B can leave its normal place. In short, a fluctuation of energy and density must take place over a region of size of the order of several (certainly more than two) atoms.

The probability of such a fluctuation is considerably less than the probability of one single atom having an abnormally high energy, and it is therefore easier to see why we do not get self-diffusion in the lattice

below the melting temperature.

In short, it is meaningless to consider the melting of single atoms. Melting is a phenomenon which necessarily involves a number of individuals. Hence one is led to deny the existence of appreciable premelting, even on the microscopic scale. The absence of macroscopically observable pre-melting follows a fortiori since the fluctuation necessary is even more improbable.

This explanation does not tell us what determines the melting temperature, but, assuming that there is a melting temperature, characterised at a given pressure by a definite value of average kinetic energy and of average inter-atomic spacing, it suggests why local pre-

melting does not take place.

The third point, viz., the sharpness of resistance change, shows that an electron does not find in the solid lattice near the melting-point that atomic disorder which characterises the liquid state and which causes its resistance to be double that of the solid in the case of the majority of metals.

On account of the large ratio of the latent heat of fusion to the specific heat (viz., about a third of the numerical value of the absolute melting temperature) the normality of the specific heat, mentioned in (4), shows that in any case the rate of change with temperature of amount (if any)

of pre-melted lattice must be very small.

Turning now to the liquid immediately above the melting-point, one notices that, since the specific heat does not differ much from that of the solid, the character of the atomic vibrations is very much the same as in the solid state, <sup>18</sup> though the frequency is probably lower. However, on melting, something in the nature of bonds between the atoms has been broken, since the compressibility of a liquid is always greater than that of a solid, even in those cases (bismuth, antimony and gallium) in which melting involves a decrease in volume. <sup>19</sup>

Finally, it may be remarked that in bismuth the orientation of a crystal is apparently not destroyed on fusion but exists in the liquid for a few degrees above the melting-point, <sup>20</sup>a conclusion which is confirmed by the observation that the thermo-electric power of a single crystal of bismuth does not alter abruptly on fusion, but gradually changes to that characteristic of the liquid, the transition being spread over a range of about 8° C. above the melting-point. <sup>21</sup>

Referring to the paper of Professor Fowler and Mr. Bernal (page 1049):

**Professor Ornstein** (*Utrecht*) said: It is obvious that Mr. Bernal is working with the Prins Zernike theory, which is a pure cluster theory for the orientation of the centres of gravity of molecules. He should also

Carpenter, Nature, 129, 60, Jan. 9, 1932.
 Bridgman, Proc. Physic. Soc., 41, 349, 1929.

Goetz, Physic. Rev., 35, 193, 1930.
 Soroos, Physic. Rev., 41, 516, 1932.

accept the orientation of the swarms. The difference is that the orientation of the swarms is governed by the continuous possibilities of orientations, whilst in the swarms in liquids the molecules are discontinuous elements. The distribution curve of the orientation would exhibit a very sharp peak if the region were of the order of the mean cluster.

Mr. G. S. Hartley (London) said: Was it considered possible for a liquid, such as water, which was not usually considered liquid crystalline, but was more highly organised than, for example, carbon tetrachloride, to consist of small aggregates possessing structure swimming about in an otherwise amorphous medium? The structure of such units must clearly be different from that of the solid state, otherwise supercooling could not occur, and would presumably be, in the case of water, one of the types suggested by Fowler and Bernal. While it was true that, from the point of view of the phase rule as ordinarily applied, such a system would be an invariant one and could not exist over a range of temperatures, it seemed to the speaker that the swarm theory also is in conflict with ordinary thermodynamics. In solid crystal structures the chemical potential decreases slightly with increasing size of crystal, and small crystals tend to go over into larger ones. Such change is very slow with crystals of at least microscopic size, but in solids the molecules are almost immobile. In a nematic liquid, however, the molecules are not much less mobile than in an ideal liquid, and the crystal units are, according to the swarm theory, of ultramicroscopic size except in the debateable surface region. We should therefore expect on thermodynamic grounds a rapid growth to larger crystals. If this does not occur because the structure is so fragile that it can be broken up by Brownian movement, the resulting equilibrium seems to necessitate the assumption that there is an optimum crystal size with minimum chemical potential, which potential must increase with increasing size beyond this optimum. A structure having this peculiar property might be capable of coexisting with amorphous liquid over a range of temperatures if the change of chemical potential with temperature also varied with size. The phase rule would have to be modified in dealing with this system since we have a variable, namely particle size, which is not normally taken into consideration, becoming important. The crystal units would have an approximately uniform size at any one temperature, but on changing the temperature they would not necessarily either disappear or grow to include the whole component, but would merely increase or decrease in size.

#### CORRIGENDA.

P. 949 (7 lines from bottom) should read:—  $= F (\cos \phi_0, \pi/2) - F (\cos \phi_0, \psi_0),$ 

P. 950 (13th line) should read:—
can be put equal to  $(\epsilon' - \epsilon_2 + \Delta \cos^2 \alpha) \ z/\epsilon^2$ .

P. 986, line 4: transpose kg./cm.², to end of line which will then read—critical point, Fig. 3. The critical values for ethyl ether are \$ 36.7 kg./cm.²,

### THE SORPTION OF VAPOURS BY NITROCOTTON.

By J. W. McBain, S. J. Good, A. M. Bakr, D. P. Davies, H. J. WILLAVOYS AND R. BUCKINGHAM.

Received 31st May, 1933.

Scientific literature contains only two papers 1 recording measurements of sorption by nitrocotton and another brief summary of the following unpublished work 2 from the chemical laboratory of Bristol University carried out in 1923-27.

#### Experiments (by S. J. G. and A. M. B.), Using the Method of Bakr and King.3

Prior to the introduction of the more accurate sorption balance, a few experiments were carried out (1923) with acetone, benzene, and

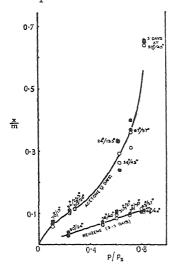


Fig. 1.—Individual sorption ("direct") and desorption ("reverse") measurements (by S. J. G.) for acetone and benzene by method of Bakr and bulb. King. Q - direct; ● - reverse. With acetone experiments at 64°-25.5° r day, at 50°-45° 5 days, remainder 2 days.

chloroform, using a modification of the method employed by Bakr and King. The apparatus consisted of a vertical glass tube, closed by a bulb at both ends, the tube being bent into a U-shape near the upper end. About 1-1.5 g. of nitrocotton was weighed into the upper bulb (10-15 c.c. capacity), the lower bulb (2-5 c.c. capacity) was filled with liquid, and after this was frozen by a mixture of solid carbon dioxide and ether, the whole apparatus was evacuated and sealed. Two electric ovens kept the upper and lower bulbs at any desired temperatures, T<sub>1</sub> and T<sub>2</sub>, respectively. The liquid was always maintained at a lower temperature than the nitrocotton, its saturated vapour thus controlling the pressure throughout the system. In a "direct" experiment the nitrocotton was initially free from sorbed material and the vapour was sorbed by it. For the "reverse" experiments the liquid was run into the upper bulb after sealing and the excess allowed to distil into the cooler lower

In these experiments evacuation of the system was carried to only 0.03-2.5 mm. of mercury.

After completion of the experiment, the upper bulb was sealed off, weighed, and analysed. If C is the volume of the free space in the upper bulb, the weight of the nitrocotton and

3 A. M. Bakr and J. E. King, Trans. Chem. Soc., 119, 454, 1921; see also A. M. Bakr and J. W. McBain, J. Am. Chem. Soc., 46, 2718, 1924; J. W. McBain, D. N. Jackman, A. M. Bakr and H. G. Smith, J. Physic. Chem., 34, 1440, 1930.

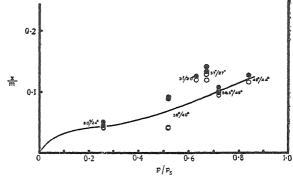
<sup>&</sup>lt;sup>1</sup> L. Rubenstein, J. Physic. Chem., 34, 2330, 1930; W. J. Jenkins and H. B. Bennett, J. Physic. Chem., 34, 2322, 1930.

<sup>2</sup> J. W. McBain, The Sorption of Gases and Vapours by Solids, pp. 371-376 (George Routledge & Sons, Ltd., London, 1932).

sorbed vapour is w - b, where w is the weight (corrected for displacement of air) of the contents of the upper bulb, and b is the weight of C

c.c. of vapour at  $T_1$ and a pressure p(the vapour pressure of the liquid at  $T_2$ ). A blank experiment in which liquid was placed in the lower bulb was carried out to correct for the air contained in the nitrocotton before evacuation.

The same specimen of nitrocotton these first experi-Samples



was used in all of Fig. 2.—Individual measurements (by S. J. G.) for chloroform as in Fig. 1, 3-5 days. ○ - direct; ● - reverse.

from it were prepared by heating thin layers in an electrical oven at 60° C. for 6 hours (12 hours in case of acetone by A. M. B.), and were then kept in a stoppered bottle in a desiccator until used.

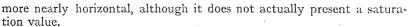
Kahlbaum's acetone stood over anhydrous sodium sulphate for 24 hours, and was then distilled. (The acetone used by A. M. B. was purified by means of the compound with sodium iodide.) Kahlbaum's benzene free from thiophene was redistilled. Medicinal chloroform was shaken with calcium chloride and redistilled.

The data are shown in Figs. 1-3, where x/m is the weight, x, of vapour sorbed by m grams of nitrocotton, and  $p/p_s$  is the relative humidity, that is, the actual pressure of vapour, p, divided by the saturated vapour

> pressure,  $p_s$ , at the temperature of the nitrocotton.

The graphs clearly show, first, that the sorption quickly leads to true, reversible equilibrium, direct and reverse experiments giving the same results. Secondly, the chief factor governing the amount of sorption of any one vapour is the relative humidity,  $p/p_s$ , which is determined by the temperature difference,  $T_1 - T_2$ 

The third important observation is the difference in the amount of sorption of the true solvent acetone and the other two substances, chloroform and benzene, in which nitrocotton does not dissolve. Far more acetone is taken up, and in particular with acetone the amount of sorption rises rapidly as the relative humidity approaches saturation and at saturation tends to become unlimited, the isotherm pointing upwards. benzene and chloroform the isotherm is



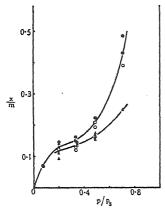


Fig. 3.—Individual measurements at 60° (by A. M. B.) for acetone as in Fig. 1, showing "consolidation" after 3 days. O - direct, 2-3 days; • - reverse, 2-3 days; △ - direct, 4-9 days; ▲ - reverse, 4-9 days.

From these facts we deduced that the important difference between solvent, incipient solvent, or non-solvent is the extent of the interaction with the solid structure. The different cases do not involve the same area of exposure or number of residual valencies participating. Indeed, the solvent itself opens up the solid structure and exposes more and more of it to attack or interaction. A liquid that is not a perfect solvent stops short before completely exposing the surface of the constituent molecules of the nitrocotton by dismembering the cell walls and even the micelles. The difference in the amounts taken up and in the behaviour in nearly saturated vapour is, therefore, attributed to a change in the structure of the solid itself brought about by the better solvent only. Thus there is no saturation value, and the amounts of different vapours taken up do not depend upon their molecular weights or actual volumes because no definite surface and no definite number of points of attachment are involved, even in one isotherm.

A fourth point, more clearly evident in Figs. 3 and 4, is that in addi-

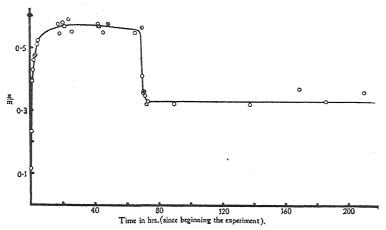


Fig. 4.—Time experiment (by A. M. B.) with sorption balance,\* nitro-cotton at 60°, acetone at 40°, showing consolidation after 3 days.

tion to a negative temperature coefficient, implying a heat of sorption distinctly greater than a mere heat of liquefaction, there is a change occurring at 50° or 60° C. which does not take place at room temperature. If nitrocotton has upon it sorbed vapour, after two or three days at 50° or 60°, some change which we may provisionally designate "consolidation" sets in whereby the amount of sorption is diminished to about two-thirds of the value which obtains both for nitrocotton containing sorbed vapour that has not been heated and for nitrocotton that has been heated but in the absence of vapour. This consolidation is clearly indicated by the position of the isotherm in Fig. 3, and is more clearly elucidated in Bakr's time experiment with the sorption balance exhibited in Fig. 4. Several experiments of up to several months' duration were carried out with the sorption balance by H. K. Harrison (1924), using nitrocotton at 60° and acetone or benzene at 14°. These showed no change with time after 4 days in the cases of benzene  $(p/p_s = 0.125)$ and acetone  $(p/p_s = 0.147)$ .

<sup>\*</sup> Evacuation only to 0.2 mm. Hg; wire spring, in this experiment only.

Before turning to results with the sorption balance, comment may be made upon the fact that in the reverse experiments liquid acetone was allowed to remain in contact with the nitrocotton for 24 hours, completely gelatinising it. Upon desorption the nitrocotton remained as a hard, yellowish, shrunken gel. The amount of sorption is (Figs. 1 and 3) distinctly greater than in the direct experiments where at lower relative humidities the nitrocotton remained fibrous, and at higher relative humidities became a hard, semi-fibrous gel. Both benzene and chloroform leave unchanged the fibrous appearance of the nitrocotton.

Had it been legitimate to apply the classical equation for capillary condensation in pores 4 to these data, the results would lead to such conclusions as the following. From acetone one would have deduced the presence of 8.5 million kilometers of pores of radius 55 Å. and 176 million kilometers of pores 4 Å. in radius in each gram of nitrocotton, whereas from benzene there would be only 0.5 million kilometers of pores of 90 Å. and 10 million kilometers of pores of 11 Å. radius, and from chloroform the same lengths of pores of 74 Å. and of 9 Å., respectively. This hypothesis, however, must decisively be rejected, because it presumes a surface tension, i.e., a negative hydrostatic pressure, whereas these liquids produce expansion of the solid.

#### Method of the McBain-Bakr Sorption Balance.

All other experiments were performed with the McBain-Bakr sorption balance <sup>5</sup> which has a great advantage over the method first used in that, the sorption balance having been set up and finally sealed, a whole series of isotherms can be obtained for one sample of nitrocotton, a feature of great importance in view of the possible slight variation of composition of nitrocotton from one sample to another, or of possible variations in dryness or impurities. The experimental method consists of enclosing o·1-o·3 g. of nitrocotton (carried in a platinum bucket suspended from a calibrated spiral silica spring) in a glass tube, together with a bulb of the liquid under investigation. The system is evacuated (the nitrocotton being meanwhile heated to 50°-60°), sealed up, the length of the spring read at 30° and sometimes at 60° to determine the weight of the nitrocotton, and then the liquid is released. By subsequent measurements of the length of the spring the amount of vapour taken up by the nitrocotton at different pressures can be determined.

The upper part of the sorption tube containing the spring and the nitrocotton was kept at a constant temperature,  $T_1$ . By maintaining the liquid in the bottom of the tube at a succession of lower temperatures,  $T_2$ , the amount of sorption by the nitrocotton at  $T_1$  would be measured over a range of pressures. The pressure throughout the tube at any time was the saturated vapour pressure corresponding to the temperature of the liquid,  $T_2$ .

When the bath temperature was above that of the room, electrical heating coils were placed around the tubes in the space between the oven and the surface of the lower thermostat to raise the temperature of this region above  $T_2$ .

In all cases the isotherms for nitrocotton at 60° were determined after completion of one or more 30° isotherms. Any further isotherms are labelled "subsequent" in the figures.

The nitrocotton was supplied in 1923 by Nobel's Explosives Co., Ltd., of Ardeer, Scotland, and was specified as follows: nitrogen, 12·27 per cent.; ash, 0·34 per cent.; solubility in ether-alcohol practically complete.

<sup>&</sup>lt;sup>4</sup> Compare J. W. McBain, The Sorption of Gases and Vapours by Solids, p. 432. <sup>5</sup> J. W. McBain and A. M. Bakr, J. Am. Chem. Soc., 48, 690, 1926.

Samples were prepared for use by heating in thin layers for 3 hours at 60° in an air oven.

Experiments of D. P. Davies 6 (1925).—Tubes were evacuated at 55°-60° for 2½-5 hours at 0.001 mm. The initial adjustment toward equilibrium is rapid but final equilibrium is rather slowly attained. Several hours were required for attainment of equilibrium when the liquid was at temperatures above 10°, but with T<sub>2</sub> below 10° as much as several days was sometimes necessary. Especially pure liquids were employed.

Comparison of the preceding isotherms with those to follow clearly illustrates the effect that has been shown by McBain and collaborators to be so striking in the case of isotherms of charcoal; namely, that as evacua-tion is improved the intial portion of the

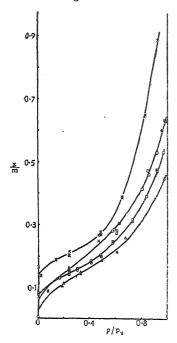


Fig. 5.—Acetone (by D. P. D.), showing opposite effects of gelatinisation and consolidation. Nitrocotton gelatinised;  $\times -30^{\circ}$ ;  $]-60^{\circ}; + - subsequent 30^{*};$ - subsequent 60°. Nitrocotton ungelatinised: O - 30°; △ -60°; • - subsequent 30°; - subsequent 60°.

isotherm for infinitesimal pressures follows more and more closely the x/m axis, the initial sorptions being far greater as impurities are removed. For reasons which will become obvious the isotherms cannot in the case of nitrocotton assume the nearly rectangular form of the ideal isotherm for charcoal.

The data are shown graphically in Figs. 5, 6 and 7. The experiments were always carried out in such order that whilst  $T_1$  was held constant,  $T_2$  was alternately raised and lowered, thus alternating sorption and desorption. The fact that all the points are represented by one curve shows the reversibility of the sorption. This is especially true of alcohol, benzene, water, chloroform, and hexane, all of which do not gelatinise nitrocotton, although alcohol does exhibit a slight gelatinising effect. The sorption is unaffected, even when any one of these liquids has been poured upon the nitrocotton. This is also true when nitrocotton has been exposed only to the vapour of the solvents, acetone and methyl ethyl ketone. Possibly, however, with sufficient time the nitrocotton might have continued its progressive shrinking and darkening upon exposure to the vapour and might finally have become completely gelatinised.

However, when the nitrocotton was flooded with the liquid solvent acetone,

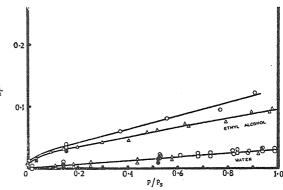
there was great shrinkage to form a coherent gel, and this gelatinised nitrocotton exhibits a higher sorption isotherm than the ungelatinised nitrocotton. At very low relative pressures the gelatinised nitrocotton takes up almost twice as much as the ungelatinised fibres. This was confirmed by H. J. W. for methyl ethyl ketone. But in spite of this, the new isotherms for the gel were again identical for sorption and desorption.

Consolidation is clearly visible with benzene, alcohol, probably water,

<sup>&</sup>lt;sup>6</sup> Chloroform, a non-solvent, gave x/m = 0.116 for  $30/25^{\circ}$  or  $p/p_s = 0.809$ .

and with nitrocotton, which has been gelatinised by contact with liquid acetone. Consolidation is either very slight or else is largely counter-

balanced by the effect of incipient gelatinisation in the case of acetone and methyl ethyl ketone where care was taken to allow the nitrocotton come into contact only with vapour and not In with liquid. both cases the experiments the same before and after taking



30°, which were Fig. 6.—Ethyl alcohol and water (by D. P. D.), showing consolidation.  $\bigcirc -30^\circ$ ;  $\triangle -60^\circ$ ;  $\bigcirc -$  subsequent  $30^\circ$ ; subsequent 60°; nitrocotton ungelatinised in all cases.

the isotherm at 30°, are not conclusive because the heating lasted less than 48 hours. There is a slight effect upon the final reheating to 60°, but the reduction is far less than in all the other cases as may be seen from the inspection of the point at the lowest partial pressure  $(p/p_s=0.17)$ where the reading was taken after 27 days with the nitrocotton at 60°, and the acetone or methyl ethyl ketone at 16.9°.

It is of interest to note that all the isotherms conform within the experimental error to the Langmuir

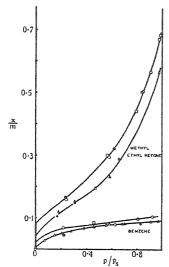


Fig. 7.—Benzene and methyl ethyl ketone (by D. P. D.). O - 30°; subsequent 6ο°; nitrocotton ungelatinised.

formula,  $x/m = \frac{abp}{1 + ap}$ , with empirical constants a and b from the origin up to the value  $p/p_s = 0.4$ , or even somewhat higher. x/m then begins to exceed the The absolute amount expected value. of this excess is minute for non-solvents, more for the semi-solvents, benzene and ethyl alcohol, and very great for the good solvents, acetone and methyl ethyl Some of the excess may be due to capillary condensation in the interstices of the fibrous powder, but the very disparity between the amounts quoted is proof that much of the excess in the case of solvent and even of semi-solvent must be due to adsorption or persorption on newly exposed surface which the vapour has itself opened up for penetration and interaction. The extra amount of acetone and methyl ethyl ketone taken up by the gelatinised nitrocotton may well be likewise due in part to capillary condensation in pores in the

semi-rigid gel. Inspection of Fig. 5 shows how very firmly the extra acetone is retained by the gelatinised nitrocotton, even when  $p/p_s$  is

reduced to 0.001 or 0.0001, where x/m is still 8 or 9 per cent. of the

weight of the nitrocotton.

For ungelatinised nitrocotton and  $p/p_s = 0.4$ , the value of x/m is for the two good solvents, acetone and methyl ethyl ketone, 0.202 and 0.216; for the semi-solvents, alcohol and benzene, 0.062 and 0.066; and for the non-solvents, water and hexane, 0.015 and (0.002).

The relative position of the isotherms yield information as to the heat of sorption. Where they are nearly together as in the curves for consolidated nitrocotton at 30° and 60°, the latent heat of sorption

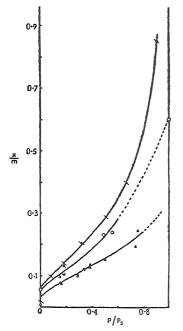


Fig. 8.—Acetone (by H. J. W.), showing opposite effects of consolidation and degradation of nitrocotton. ○ - 30°, ungelatinised, non-consolidated nitrocotton; △ - 60°, ungelatinised but consolidated nitrocotton; - 60°, degraded nitrocotton, previously recovered from solution in acetone; ★ - 60°, nitrocotton previously heated alone or 24 days at 60° before use

must be equal to that of the latent heat of condensation of vapour to liquid. With acetone, however, this is definitely exceeded. Were the consolidation to be neglected, the heats of sorption calculated would in all cases appreciably exceed the heats of condensation, most of all for the two good solvents, acetone and methyl ethyl ketone. The initial sorptions are attended by a greater heat than subsequent amounts. experiments with acetone with ungelatinised fibres, the molar heat of sorption declined from 10,150 to 8170 calories as compared with the latent heat of 7200 calories; similarly, for methyl ethyl ketone 10,720 calories fell to 9309 calories for higher  $p/p_s$  as compared with 6230 calories.

Experiments of H. J. Willavoys (1926).—The experiments 7 were now extended to include methyl alcohol, toluene, pentane, and chloroform as well as experiments with acetone upon nitrocotton that had been subjected to various preliminary treatments. periments on the effect of soaking the nitrocotton in the various liquids included also benzene and methyl alcohol. Given sufficient time desorption ultimately agreed with sorption except, of course, where the position of the isotherm had been permanently shifted through gelatinisation. Slight gelatinisation occurred with methyl alcohol.

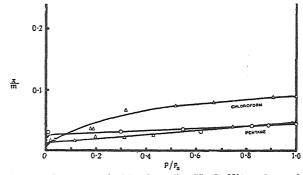
The progress of consolidation was directly observed with acetone at 60°. Curves with acetone are reproduced in Fig. 8 in order to compare the isotherm for non-gelatinised but consolidated nitrocotton with that for non-gelatinised, non-consolidated nitrocotton which had been heated for 24 days at 60° previous to exposure in the sorption experiment. One point only is recorded, but it shows conclusively that mere prolonged heating of dry nitrocotton at 60° does not affect its sorbing

<sup>&</sup>lt;sup>7</sup> Evacuation of the tubes lasted from 3-4 hours and reached a value slightly less than o ooi mm.

capacity for acetone and does not consolidate it. Such nitrocotton is, however, distinctly degraded.

It is well known that nearly every experience undergone by cellulose

and its derivatives tends towards "degradation" as is evidenced by the progressive decrease in the viscosity of solutions made from them.8 It is commonly assumed that this degradation is a breaking down of the physical or even chemical structure of the cellulose.



even chemical Fig. 9.—Pentane and chloroform (by H. J. W.).  $\bigcirc -30^\circ$ , structure of the nitrocotton ungelatinised before and after treatment with liquid;  $\triangle -60^\circ$ , ungelatinised.

Nitrocotton which has been dissolved in acetone and used for some time in viscosity experiments and then recovered by evaporating off the solvent and kept at 60° in vacuo for 28 days is certainly degraded. Nevertheless, its sorptive capacity is increased as is apparent from inspection of Fig. 8 where the top isotherm refers to such recovered nitrocotton. This shows directly that consolidation is not degradation, but some different phenomenon which has not hitherto been related to any other property of the cellulose derivatives, being completely un-

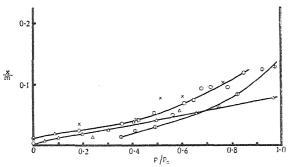


Fig. to.—Methyl alcohol (by H. J. W.), showing effect of progressive gelatinisation and also the effect of long standing at room temperature in saturated vapour.  $O = 30^{\circ}$ , nitrocotton ungelatinised;  $\times = 30^{\circ}$ , gelatinised;  $\triangle = 60^{\circ}$ , ungelatinised;  $\square = 60^{\circ}$ , gelatinized;  $\square = 50^{\circ}$ , gelatinized;  $\square = 50^{\circ}$ , isotherm 8 surprise to see how months later (R. B.) after a second intervening treatment little methyl alcohol.

suspected. Consolidation may possibly be due to a recoupling such as is referred to in the previous footnote.

The new data for chloroform and pentane are given in Fig. 9, where it is surprising to see how much pentane is taken up. Likewise, in Fig. 10 it is again a surprise to see how little methyl alcohol is taken up at

all the lower ranges of relative pressure.

The new data for toluene and benzene are not reproduced because

<sup>8</sup> The first exception to this rule was found by J. W. McBain, C. E. Harvey and L. E. Smith (*J. Physic. Chem.*, **30**, 312 (1926), who found that under certain circumstances nitrocotton could be recoupled or built up again to give solutions of higher viscosity than that of the original specimen. In criticism, the improbable surmise has been advanced that the result was merely fractionation.

<sup>9</sup> E. O. Kraemer and G. R. Sears (*J. Rheol.*, **2**, 299, 1931) found that sorption from solution was independent of the viscosity characteristics of nitrocellulose, as shown by experiments with acetone and heptane, and cellosolve and benzene.

of their resemblance to those previously given for benzene, but they may be characterised by pointing out the importance of consolidation. For consolidated nitrocotton at 60° the two solvents are almost indistinguishable at lower relative pressures, but benzene exceeds toluene at higher pressures :---

$p/p_{s}$ $C_{8}H_{6} x/m$ $C_{7}H_{8} x/m$	0·1 0·022 0·026	0.034	0.042	0.050	0.058	0.067	0.076	0.084	o·9  o·068	0.075
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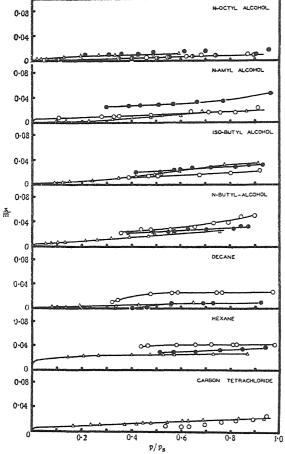


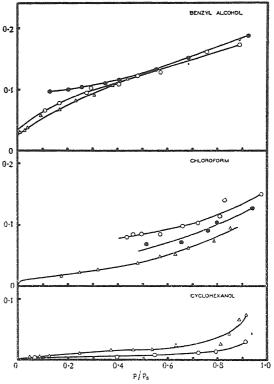
Fig. 11.—Poorly sorbed vapours (by R. B.).  $\triangle - 60^{\circ}$ ;  $\bigcirc - \text{subsequent}$  30°;  $\bigcirc - 30^{\circ}$ , O - 30°; △ - bo; — - subsequent 30, , after previous 30°; nitrocotton ungelatinised in all cases. one month

30° Αt the most noteworthy point is the manner in which the isotherm retains a much higher value down to very low relative pressures, therefore making almost rectangular change of direction at the left-hand side of the diagram.

Experiments of R. Buckingham (1927.) - Using still better evacuation of the nitrocotton (10-4  $10^{-5}$  mm. of mercury for  $3\frac{1}{2}$ hours). the measurements were extended to a large number of liquids. Again, to save space, the detailed data are presented in graphical form, Fig. 11 being a composite made by superimposing the diagrams for all the vapours sorption was least. Likewise, Figs. 12

and 13 present those with moderate amounts of sorption, while those with highest sorptions ever observed are assembled in Fig. 14. In viewing these diagrams, it should be remembered that the original graphs for all the diagrams in this paper were plotted with identical scales both of  $p/p_s$  and of x/m. In the reproduction, the proportions in each diagram are, therefore, retained, but the absolute size is greatly altered. Hence the amount of sorption in different diagrams should be

estimated by comwith parison the width of the diagram, that is,  $p/p_s$  which in each case covers the same range, zero to unity. Thus a tall narrow diagram portrays great sorption; a square one, medium; and a low broad diavery little gram, sorption. The actual scales are, of course, given in each case. Fig. 14 includes for comparison data for the excellent solvent acetone. For the experiments by R. B. no records of time and date were available, and it is not certain in how far the conditions emerging from the previous investigations were observed.



#### The most notice- Fig. 12.—Sorption experiments (by R. B.), showing consolidation with chloroform and progressive gelatinisation with benzyl alcohol. ○ - 30°, ungelatinised; △ - 60°, ungelatinised; - subsequent 30°, ungelatinised

#### Discussion.

able feature is that the sorption of twentythree different vapours

ranges from values as low as about I per cent. of the weight of the nitrocotton for indifferent liquids such as water and the paraffins up to 100 per cent. or more for the excellent solvents such as the ketones and acetates. For the sake of comparison, the values obtained in isotherms at 30° with unaltered nitrocotton as far as available are collected in Table I. Since for the acetates the fibres certainly become gelatinised at the higher relative pressures, two sets of values are given for the ketones, the first those obtained in precisely the same manner as with the acetates and, secondly, the lower values from experiments in which more care was taken to minimise gelatinisation.

It is quite clear that the good solvents for nitrocotton are extensively sorbed, whereas those substances which in liquid form have no noticeable effect upon nitrocotton are correspondingly poorly sorbed. Those which show incipient gelatinisation or cause some hardening or coalescence of the fibrous powder occupy an intermediate position. The acetates and ketones here mentioned are solvents outright; methyl alcohol barely disperses the nitrocotton, producing a soft or flowing gel; ethyl alcohol, unless chilled or admixed with other substances (which may include non-solvents), merely produces a semi-transparent gel.

The acetates and ketones at high relative humidity are taken up ten times as much as the following group in Table I, although these themselves are taken up from five to ten times as much as the remainder of the list. Within any one homologous series, increase in molecular weight usually diminishes sorption, especially when sorption is expressed in number of mole sorbed, and particularly at higher relative pressures. This may be due primarily to the small size of the interstices into which the molecules have to thrust themselves and partly to lessened affinity. Taking a methyl group from the end position in butyl alcohol and placing it on the side of the molecule diminishes sorption as seriously as if the

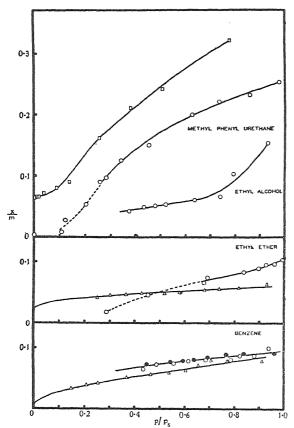


Fig. 13.—Sorption experiments (by R. B.), showing gelatinisation with methyl phenyl urethane. ○ - 30°; △ - 60°; ● - subsequent 30°; nitrocotton ungelatinised. □ - 60°, gelatinised.

chain had lengthened to form n-amyl alcohol. The combination of benzene ring the and the alcohol grouping enhances the sorption above either separately. Saturation, by using hexamethylene ring for a benzene ring, as in cyclohexanol largely eliminates sorption.

It follows from these and other observations, such as those on viscosity, tolerance to precipitating admixswelling of tures, films in various liquids and liquid admixtures, etc., that there are deof solvent grees power ranging from zero to complete solution. would, therefore, term the acetates and ketones good or very good, methyl phenyl urethane, methyl and ethyl

alcohols moderate, substances such as chloroform, benzene, toluene, and ether semi-solvents, and rank the rest as poor or very poor in respect to solvent action.

The second point, which is recurrent throughout the description of the experimental work, is that if the nitrocotton contains sorbed vapour and is maintained at 60° for at least 4 days, "consolidation" sets in with the corresponding diminution 10 of the sorbing power to about two-thirds of its previous value whether at 60° or 30°. This is clearly seen

with all the substances in Table I for which opportunity was given, down to and including n-butyl alcohol.

The term consolidation may not at first seem particularly well chosen. However, it conveys two ideas which seem to justify its use. In the first place, the amount of sorption is, in fact, diminished. No matter what hypothesis may be favoured as an explanation of sorption,

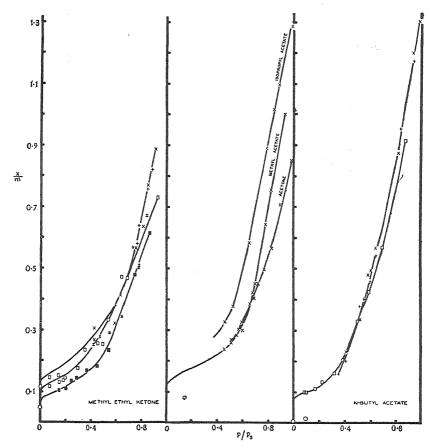


Fig. 14.—Excellent solvents (by R. B.), including methyl ethyl ketone (by H. J. W. with subsequent measurements by R. B.).  $\bigcirc -30^\circ$ , nitrocotton ungelatinised.  $\times -30^\circ$ ;  $\bigcirc -60^\circ$ ;  $\uparrow -$  subsequent  $30^\circ$ ; \* — subsequent  $50^\circ$ ;  $\uparrow -$  second subsequent  $30^\circ$ ; nitrocotton gelatinised in all cases.

the classical compressed film, capillary condensation, or one of Langmuir's monomolecular types, lessening of surface would serve to explain lessened sorption. In the second place, we incline to the view that with nitrocotton exposed bonds may be coupled to each other, thus consolidating the residue and lessening the number of points of attachment for solvent molecules.

<sup>\*</sup> In the case of n-butyl acetate this isotherm was obtained  $4\frac{1}{2}$  months after the  $60^{\circ}$  isotherm.

<sup>&</sup>lt;sup>10</sup> Miss R. R. Murray (*J. Physic. Chem.*, **20**, 621, 1916) found that cellulose (filter paper) takes up HCl from aqueous solution, but gives off half of it again within a week or ten days.

TABLE I.—Sorption of Vapours in "Per Cent." by Weight (100 x/m) by Fibres of Nitrocotton at 30° at Typical Relative Pressures,  $p/p_s$ .

Substance.		0.1.	0.3.	0.2	0.7.	o <sup>1</sup> 9.
n-Butyl acetate . Isopropyl acetate .		paradicide.	15	3 <sup>2</sup> 35	66 68	108
Methyl acetate .	:		Minamore	26	46	102
Methyl ethyl ketone			-	30	49	86
Methyl ethyl ketone			18	25	37	56
Acetone				25	42	70
Acetone				24	34	51
Methyl phenyl urethane		1 6	II	I 7	21	24
Benzyl alcohol .		6	10	12	15	17
Ethyl alcohol .		3	5	6	8	13
Methyl alcohol .		3 2 —	5 3	<b>5</b> 8	8	13
Chloroform				8	10	13
Benzene *			7	8	9	10
Ethyl ether				5 3	7	9.1
Pentane		3	3	3	4	4
Hexane				2	2.1	2.2
Decane				1.2	1.0	1.6
Water		0.8	0.9	1.6	2.2	2.7
Cyclohexanol .	•	0.4	0.5	0.7	1.3	2.7
Carbon tetrachloride			Profession .	0.7	1.3	2.3
n-Butyl alcohol .	•		2	2.7	3.6	5.0
Isobutyl alcohol .			1	1.3	1.8	2.1
<i>n</i> -Amyl alcohol .	٠	o·8	1.0	1.3	1.7	2.0
n-Octyl alcohol .		0.3	0.4	0.6	0.8	1.0

<sup>\*</sup> For a comparison of benzene and toluene, showing their similarity, although with consolidated nitrocotton, see p. 1094.

The formation of a gel is observed to increase the apparent sorption. in some cases only slightly, in others so much as quite to outweigh the effect of consolidation. This we ascribe to capillary condensation of liquid in the structure which has previously been expanded by sorption.

The sorption proper acts by satisfying the exposed valencies and by dismembering the structure through satisfying residual valencies which previously held the structure together, or were inaccessible. Capillary condensation alone cannot, of course, expand a structure on account of the tension or negative hydrostatic pressure which is associated with the concave menisci which make it possible at relative pressures,  $p/p_s$ , less than unity. The expansion, therefore, is due to sorption, and capillary condensation is a secondary phenomenon occurring in pores created by the positive forces of sorption. The greater part of the vapour is taken up by true sorption, even in the case of the best solvents at high relative humidities.

The foregoing interpretation is borne out by the fact that a graph of the sorption with the better solvents according to either the Langmuir or the Williams-Henry formula gives, at lower relative humidities, a good straight line (true adsorption), which rather abruptly changes to a slope in the opposite direction at higher relative humidities. presents a parallel with the combination of adsorption and capillary condensation observed by Bray and Draper 11 for the sorption of water vapour on certain partially hydrated oxides of copper and manganese. The difference here is that adsorption itself also opens up further portions of the nitrocotton for the sorption of good solvents.

<sup>&</sup>lt;sup>11</sup> W. C. Bray and H. D. Draper, Proc. Nat. Acad. Sci., 12, 295, 1926.

Thus, in a few cases, e.g., amyl alcohol, the 30° isotherm obtained after taking a 60° isotherm lies higher than the original 30° isotherm. This is probably attributable to some gelatinisation. In the case of isobutyl alcohol, this is very clearly shown in the 60° isotherm itself which at higher relative pressures steadily rose until it surpassed the 30° isotherm in spite of the difference in temperature. With carbon tetrachloride, cyclohexanol, and octyl alcohol the 60° isotherm seems to be higher than the 30° isotherm, but the sorption is so small that this may be ascribed to experimental error.

In some cases, no consolidation is apparent, or, in other words, the 30° isotherms before and after taking a 60° isotherm are sensibly the same (benzene (R. B.), benzyl alcohol, methyl alcohol). This may plausibly be ascribed either to insufficient time being allowed at 30° originally for equilibrium or at 60° for consolidation, or to the masking effect of incipient gelatinisation.

In two cases, methyl ethyl ketone and methyl alcohol, it was shown that a gel of consolidated nitrocotton could be shrunk by reheating to 60°, thereby diminishing its apparent sorptive power when subsequently tested at 30°. The diminution would be largely at the expense of capillary liquid.

There is no trustworthy evidence that consolidated nitrocotton reverts to its original state.

Jenkins and Bennett <sup>12</sup> showed that the sorption of acetone was dependent upon the percentage of nitrogen in the cellulose nitrate, being nearly 39 per cent. for the optimum at 12·0 per cent. nitrogen, when the nitrocotton was at 30° and the acetone at 20° C. The original cotton linters sorbed 2·5 per cent. acetone. Since the sorption proceeded for at least a day, they interpreted it as solution. However, examination of any of the numerous graphs in the present communication shows that the vapour pressures above nitrocotton containing different amounts of any one of the liquids used differ widely in their course from the typical forms for solution, homogeneous chemical equilibrium, and phase rule, respectively. They must, therefore, be interpreted in terms of sorption or persorption as we have done. It must, however, be remembered how similar the environment of a persorbed molecule, whether held chemically or physically, is to that of a molecule in solution.<sup>13</sup>

Rubenstein <sup>14</sup> confirmed that the optimum nitrogen content for sorption was 12 per cent. or slightly less, using acetone, methyl and ethyl acetates, and methyl ethyl ketone, but with methyl alcohol the sorption steadily diminishes with increasing content of nitrogen. <sup>15</sup> Rubenstein also detected an alteration which we have referred to as consolidation. Both Jenkins and Bennett and Rubenstein find that the extent of sorption is governed by nitrogen content and very little by difference in viscosity for a given nitrogen content. Their data and their findings fit in well with the data and interpretations of the present paper. Recently, very similar conclusions have been arrived at by Filby

<sup>&</sup>lt;sup>12</sup> W. J. Jenkins and H. B. Bennett, J. Physic. Chem., 34, 2323, 1930.

<sup>13</sup> Compare J. W. McBain, The Sorption of Gases and Vapours by Solids, 64.

p. 64.

14 L. Rubenstein, J. Physic. Chem., 34, 2330, 1930.

15 This "seems to be similar to the discovery of Will (Mitt. Centralst. und wiss. tech. Unters., No. 4, 1-33, 1904) that the hygroscopicity added to the nitrogen content is constant for stable nitrocotton." Possibly alcohol and water are held in the same places as nitro groups, but there is equal evidence for the different view that they may be held by nitro groups.

and Maass 16 for the sorption of water vapour by cellulose. A similar explanation would apply to the results presented by Barkas. <sup>17</sup> A parallel interpretation applies in the recent study of glyptal resins and of cellulose acetates by Winning and Williams. 18

Again, Sheppard and Newsome 19 found that the first part of the sorption of water vapour by cellulose consists of the attachment of polar molecules to cellulose hydroxyls which are not mutually satisfying each other. A further portion is held as capillary liquid, the pore space varying with the amount of sorption itself. The initial heat of sorption of water vapour by cellulose is greater than the heat of condensation, and then gradually approaches the latter. It is asserted that sorption by a completely acetylated cellulose with no free hydroxyls would be mainly a process of condensation in capillary spaces. They also studied the homologous series of alcohols with cellulose acetate, and although the results are rather irregular, they interpret them as decreasing with increasing number of carbon atoms when expressed in mols. per gram of cellulose acetate, but becoming very approximately constant above u-butyl alcohol.

# Summary.

- I. Studies of the amounts of different liquids retained by nitrocotton in equilibrium with various pressures of their vapours show a range of 100-fold between the best solvents through moderate solvents to the most indifferent non-solvents.
- 2. At lower relative pressures, sorption laws are followed, but as they increase the structure is opened up, sorption increasing, and when pores are thereby produced, capillary liquid condenses therein.
  - 3. Gels have more pore space than ungelatinised fibres.
- 4. When nitrocotton containing sorbed vapour is heated for three or four days at 60°, some change occurs, here termed "consolidation," that diminishes the sorptive power of the nitrocotton. "Consolidation" is not parallel (in its effect upon sorption) to the well-known degradation of cellulose and its derivatives.
- 5. The data do not agree with any of the single hypotheses of (a) solution, (b) heterogeneous chemical equilibrium, (c) the interpretation of sorption by the compressed film hypothesis, or (d) capillary condensation; but the predominating factor is true adsorption or, rather, persorption of the Langmuir type (compare paragraph 2 above).

We have great pleasure in acknowledging the invaluable support of Messrs. Nobel's Explosives Co., Ltd., and the unfailing interest of their scientific staff.

Department of Chemistry, Stanford University, California.

16 E. Filby and O. Maass, Can. J. Research, 7, 162, 1932; see also F. T. Pierce, J. Textile Inst., 20, 133T, 1929.

17 W. W. Barkas, Nature, 130, 699, 1932.
 18 C. H. Winning and J. W. Williams, J. Physic. Chem., 36, 2915, 1932.
 19 S. E. Sheppard and P. T. Newsome, J. Physic. Chem., 33, 1817, 1929; 34, 1158, 1930; 36, 930, 2312, 1932; compare S. Ogouri and M. Nara, J. Soc. Chem. Ind. Japan, 33, Suppl. binding 267, 1930.

## CALCIUM ACETATE GELS.

By HERBERT HENSTOCK.

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The gels, formed by a number of organic substances, appear as unstable intermediate stages between sol and crystalline solid. In course of time they change, like the coagel of soap, into crystalline masses, together with the saturated solution. Hatschek 1 showed that the gel of camphoryl phenyl thio-semi-carbazide was one of this kind, as is also that of 5-dimethyl-amino-anilo-3-4-diphenyl cyclopentene-1-2-dione described by Hardy, who found that a whole series of liquids form suitable dispersion media, and that the gels so formed have their various degrees of stability. Similar ones are produced by some cotton dyes, e.g. cotton red and chrysophenin, which have been investigated by Haller.<sup>3</sup> present ones are very similar in general properties to the ones above, but differ in that they are formed by metallic salts and are more nearly allied to the gels of uric acid salts examined by Schade and Boden, see also Bechold and Zeigler,<sup>5</sup> as well as to the jellylike solidification of solutions of Barium malonate in methyl alcohol obtained by Flade,6 and to an aqueous gel mentioned by Doehle and Rassow 7 as occurring when a solution of benzo-thiazole-methane sulphide calcium sulphonate is added to one of mercuric chloride; and lastly to the inorganic gelatinous sulphates and phosphates prepared by Neuberg and his co-workers.8

### Aqueous Gels.

The first of this series was discovered when an attempt was made to purify calcium acetate, obtained from another experiment, by precipitating it from a concentrated aqueous solution on the addition of absolute alcohol. Instead of the expected crystalline salt, a translucent, but not quite transparent jelly appeared. This exhibited a faint bluish fluorescence, probably due to incipient crystal formation, since it disappeared when the crystals became visible. On repeating the experiment with pure calcium acetate the transparency was enhanced, but it was never sufficiently clear to enable the optical properties to be observed with any degree of accuracy. The gel formed in globules the instant that the alcohol was added; these globules were transparent, but after a short time, when they coalesced, they produced an opaque mass, which, on standing for some hours, exhibited Syneresis and exuded a liquid consisting of part alcohol and part water. If alcohol is added to a hot solution of the salt, syneresis does not occur and the gel is no longer translucent and crystals soon begin to form in it. This is to be expected, since calcium acetate is more soluble in cold than in hot water. After standing for 24 hours the gel began to liquify and part of the salt

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    Kolloid Z., 11, 158, 1912.
    Kolloid Z., 22, 49, 1918.
    Biochem. Z., 20, 205, 1909; and 64, 479, 1914.
    Z. anorg. Chemie, 82, 175, 1913.
    Berl. Berl. Akad. Wiss., 45, 820, 1907.

Proc. Roy. Soc., 87A, 29, 1912.
4 Z. physiol. Chemie, 83, 347, 1913.
7 Kolloid Z., 12, 71, 1913,
8 Ber. Berl. Akad. Wiss., 45, 820, 1907.
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crystallised out in contact with the saturated solution, the three phases remaining together for some time.

The composition was estimated both from the gel itself and from its components. The solubility of calcium acetate is  $43.6~\rm g.$  in 100 g. of water at 15°; but when alcohol was added to this solution part of the salt was thrown out in crystals dispersed through the gel: this was avoided only by doubling the dilution. Using this solution, sufficient alcohol was added to produce a gel with no excess liquid. The results in molecular proportions were

Calcium Acetate. Water. Alcohol.

158 g. (1 mol.) 725 g. (40 mols). 1141 g. (24 mols).

Another portion, similarly made up, on distillation to dryness gave: Calcium acetate 158 g., alcohol water mixture 1866 g., and on taking the specific gravity of this liquid it gave roughly: water 720 g., alcohol 1140 g.

The solubility in water at 20° was 156.75 g. of gel in 100 g. of water, so that just sufficient water was present to effect complete solution.

A little, smeared on a microscope slide and viewed immediately through a I inch objective, appeared quite clear, but in a few moments long, straight, colourless, hair-like crystals began to form and soon produced a felted mass: in less than one minute these dissolved in the liquid, which had formed simultaneously. Rapid evaporation of the alcohol would occur on the thin film; this would cool the solution and help crystallisation, but a point would soon be reached where the aqueous alcohol became so weak that the crystals would redissolve.

Calcium acetate is insoluble in the monohydric saturated alcohols, and also in all the usual organic solvents. Many of these, which are miscible with water, will act as dispersion media, and therefore the gel must be insoluble in certain concentrations of these aqueous solutions.

No gels were produced with the formate, proportionate, n-butyl-rate or iso-butyrate of calcium and in consequence this peculiarity of calcium acetate might be used to distinguish the acetate ion from those of the above acids, even in the presence of their calcium salts, since these do not inhibit gel formation unless present in very large proportion.

Again, none of the acetates of the common metals, especially the alkali and alkaline earth metals, form gels by this method: strontium and barium acetates are precipitated at once in a crystalline condition. Similarly, therefore, the colloid might be used as a confirmatory test for calcium.

Those liquids, which form gels, are of course miscible with water and include the lower aliphatic alcohols, except methyl alcohol, acetone, ethyl acetate and ethers.

Glycerol, aldehydes, aniline, pyridine and phenol are inactive. Small quantities of substances tending to inhibit gel formation are dilute HCl, NaOH and  $\mathrm{NH_4OH}$ : those having no action are dilute HNO3, acetic acid and salts having no chemical action.

The electrical conductivity of the gel, made with ethyl alcohol, in the proportions already given, was  $K = 0.1904 \times 10^{-3}$ ; that of the aqueous solution of calcium acetate of like strength  $K = 0.2775 \times 10^{-2}$ . The significance of these figures will be discussed under the gels formed with methyl alcohol.

None of these aqueous gels persist for more than 48 hours at 15°, the length of time of persistence depending upon the precipitant used and the quantity present: these times vary from a few minutes to 24 hours in most cases.

A few of the various metallic salts of other organic acids have been examined but so far the only one found to give an aqueous gel of this type is sodium benzoate. This is being investigated, and it is hoped shortly to communicate the results.

# Methyl Alcohol Gels.

It is a well-known fact that calcium acetate is insoluble in ethyl alcohol, but as to its solubility in methyl alcohol no mention was found in the literature. Since no aqueous gel was produced by methyl alcohol, it was suspected that the salt might be soluble in it; this proved to be the case. The solubility of the anhydrous salt in boiling methyl alcohol was determined by withdrawing 5 c.c. in a pipette, discharging into a stoppered, weighed bottle and weighing when cool. After evaporating the alcohol and heating at 130° for 2 hours the residue was weighed. Found 1.01 g. of salt are soluble in 100 g. of methyl alcohol at 66°. Similarly, an excess of the anhydrous salt was shaken in a closed tube with cold methyl alcohol at intervals for 4 hours and the same procedure adopted. Found 0.7575 g. of salt dissolve in 100 g. methyl alcohol at 15°.

The excess calcium acetate in this latter experiment gradually increased in bulk until it occupied more than double its original volume and formed needle crystals, which had evidently absorbed alcohol. The salt was obtained in a similar condition on recrystallisation from the boiling alcohol. Both yielded the same figures on analysis. Found 0.2 g. of calcium acetate crystals lost 0.033 g. on heating at 110° = 16.5 per cent.

requires 16.8 per cent. These crystals appeared to be monoclinic prisms. Attempts to form a gel with either of the above concentrations of the salt were not very successful, but quite solid, elastic, water-clear ones set, when excess of anhydrous calcium acetate was boiled with methyl alcohol for about 30 seconds and the solution filtered and cooled. The concentration of the salt was 0.553 g. in 100 g. of methyl alcohol. To this was added about twice its weight of any one of the following liquids: (1) The normal or isomeric fatty saturated alcohols up to heptyl alcohol, except ethyl alcohol; (2) any of the corresponding simple ethers, or (3) esters; (4) benzene or toluene; (5) ethyl benzoate. These gels persisted for varying periods from 48 hours to 6 months if kept in closed vessels. Thinner gels formed with (1) aniline; (2) methyl salicylate; (3) ethyl aceto acetate; (4) ethyl and methyl iodides; (5) benzyl alcohol; (6) geraniol; (7, dibenzyl ether; (8) anisol; (9) chloroform; (10) carbon tetra chloride; (11) ethyl alcohol. No gels formed with (1) aliphatic hydrocarbons; (2) phenols; (3) glycerol; (4) all aldehydes; (5) pyridine; (6) acid chlorides; (7) pinene or limonene. A very permanent and clear jelly results with one volume of calcium acetate solution in methyl alcohol on addition of about two volumes of an equivolume mixture of benzene or toluene and isopropyl alcohol.

In order to elucidate the question as to whether water is necessary for the formation of these colloids, all materials and apparatus were very thoroughly dried by appropriate methods, but no difference was noted, therefore they can be formed without water; and in this respect they are like those described by Hardy.<sup>2</sup> Like the aqueous ones, they commence to form as soon as the precipitants are added, but not becoming solid quite so rapidly, they allow more time for observation. From invisible nuclei, transparent globules, like small frog spawn, form first and float about in the liquids: these rapidly grow in size until they touch each other; the surface films being still visible. In 10 or 15 minutes they coalesce to solid, water-clear jellies. If too little precipitant

is added, solidity is not attained, if too much, some of the salt is thrown out in a crystalline condition. When kept for varying periods in open vessels, the liquids evaporate and leave solutions, in which float crystals of calcium acetate. Excess alcohol or precipitant is not absorbed by these colloids, which do not swell; they are non-elastic gels. Substances tending to destroy them or inhibit their formation are: (I) Many inorganic salts soluble in methyl alcohol; (2) acids; and other substances already mentioned. Inactive are (I) Iodine; (2) caustic soda (trace).

Some of their physical properties yielded results of interest.

Heat.—They may be kept at 100° for 2 or 3 hours without alteration, but at higher temperatures, i.e., between 120° and 150°, the exact temperature depending upon the precipitant, they break down, and the resulting liquids are suddenly vaporised, blowing the jellies out of the containing vessel to a height of 2 or 3 feet.

Penetration by most coloured salts is precluded, owing to their inhibiting effects, and the same applies to some of the dyestuffs. Halian-

thene penetrated 11 inches in 24 hours.

Liesegang Rings are difficult to obtain for a similar reason. One ring and an incipient second one formed with dimethyl glyoxime in the

gel, and nickel chloride above.

Bubble formation may be effected by gently shaking the sols with air when adding the precipitant. As maximum solidity is being attained, these bubbles swell to I or 2 mm. in diameter. They are not spherical, as would be the case in a liquid, but definitely spheroidal, some being almost lens-shaped, yet they are not oriented in any particular direction (photograph No. I). This absence of regular orientation is due to the bubbles being in the liquid between the gel nuclei, which catch them in varying positions as the globules touch each other. The spheroidal shape is produced by pressure, exerted by the gel itself; this pressure must be greater in some directions than in others, indicating that the gel is not completely isotropic. Lens-shaped bubbles have also been recorded by Hatschek, who unsuccessfully tried to find whether the lens planes showed pressures in any particular directions and so determine any lines of cleavage.

Optical Properties. Double Refraction.—Irregular faint bands were seen between nicol prisms. They changed through the usual colour series on rotating through 90°, and became slightly stronger under pressure. There is, therefore, weak double refraction of the kind

inherent in the gel itself.

Polarised Light.—In a tube 1 cm. in diameter and 20 cm. long, a gel made with *di-iso*-amyl ether, which yields a very clear one, produced a rotation of + 0·46° with sodium light  $\lambda = \cdot 5893$  at 20°.

Refractive indices of a number of these gels were taken with a Pulfrich refractometer, using sodium light as above. The results are given in column 2 of the table.

Because the sols changed so rapidly, it was found to be impossible to take their refractive indices before they solidified to gels, and so the figures were calculated from those of each member of the mixtures.

A kind of regularity, which serves to connect index of refraction with density, concerns the specific refractions of the solutions of electrolytes and of their components. Of the various expressions for specific refraction in common use, the best known and the most satisfactory are those

of (I) Gladstone and Dale 10 and of Lorenz 11 and Lorentz. 12 Using the latter equation, the specific refraction

$$K = \frac{\mu^2 - 1}{\mu^2 + 2} \times \frac{1}{\rho} \quad . \tag{1}$$

The law of mixtures has been found by Biot and Arago to hold very closely for the specific refractions of solutions and their components in

$$K_e + K_w(100 - x) = K_s 100$$
 . (2)

Combining (1) and (2)

$$K = \frac{1}{x} \left( \frac{\mu_s^2 - 1}{\mu_s^2 + 2} \times \frac{100}{d_s} - \frac{\mu_w^2 - 1}{\mu_w^2 + 2} \times \frac{100 - x}{d_w} \right) . \tag{3}$$

Values found.

K = the specific refraction of the salt in solution. where

x = per cent. of salt..

 $\mu_s = \text{index of refraction of the solution at 20}^{\circ}$ 

 $\mu_w = \text{index of refraction of methyl alcohol at 20}^{\circ}$  . I · 3274

 $d_s = ext{density of the solution at 20}^\circ$  . .  $d_w = ext{density of methyl alcohol at 20}^\circ$  . .

TABLE I.—Refractive Indices of Gels made from a 0·553 Per Cent. Solution of Calcium Acetate in Methyl Alcohol.  $T=20^\circ.$ 

Made with	2 Vols of	f	Refractive Indices of Gels.	Refractive Indices of Sols. (Calculated.)	Differences.	Increments for Rise of CH <sub>2</sub> .	Mol. Wt. of Precipitants.
n-propyl alc	cohol		1.3775	1.3709	0.0066	8	60
n-butyl	,,		1.3866	1.3792	0.0074		74
n-amyl	,,		1.3933	1.3848	0.0083	9	88
n-hexyl	,,		1.4025	1.3914	0.0031		102
n-heptyl	,,		1.4073	1.3975	0.0098	7	116
iso-propyl	,,		1.3671	1.3638	0.0033	8	бо
iso-butyl	,,		1.3828	1.3787	0.0041		74
iso-amyl	,,		1.3898	1.3849	0.0049	8	88
acetone (1 v	ol.)		1.3566	1.3500	170		58
CCl <sub>4</sub> (3 vols.	.)	٠	1.4875	1.4015			154

Assuming that the specific refraction of calcium acetate and that of methyl alcohol are additive in K, its value was 1.75. This equation holds for only one liquid as solvent. In the case of the sols, the physical properties of the second and third liquids must be introduced, as additive

<sup>10</sup> Phil. Trans., 887, 1855.

<sup>12</sup> Ibid., 9, 642, 1880.

<sup>&</sup>lt;sup>11</sup> Wied. Ann., 11, 70, 1880.

properties, into the term  $d_s$  and on expanding to include the second liquid, we have

$$K = \frac{\mathrm{I}}{x} \left( \frac{\mu_s^2 - \mathrm{I}}{\mu_s^2 + 2} \times \frac{300 \cdot 55}{d_s} \right) - \frac{\mathrm{I}}{x} \left( \frac{\mu_w^2 - \mathrm{I}}{\mu_w^2 + 2} \times \frac{100}{d_w} \right) - \frac{\mathrm{I}}{x} \left( \frac{\mu_\mathrm{A}^2 - \mathrm{I}}{\mu_\mathrm{A}^2 + 2} \times \frac{200}{d_\mathrm{A}} \right) \ (4)$$

where  $\mu_A$  = the refractive index of the precipitating alcohol and  $d_A$  its density.

Substituting 1.75 for K, the values of  $\mu_s$  appear in column 3 of the table: these are all lower than those in column 2, indicating a rise in refractive index between sol and gel. The increment of rise is nearly 0.0008 for each  $\mathrm{CH_2}$  rise in the molecule of the precipitant, and is therefore a function of its molecular weight.

The electrical conductivity at 25°, for a gel made with toluene, was  $0.939 \times 10^{-5}$ ; for a 0.533 per cent. solution of calcium acetate in methyl alcohol it was  $0.6954 \times 10^{-4}$ , and for methyl alcohol  $0.244 \times 10^{-5}$ . The value for the calcium acetate solution is more than seven times greater than that of the gel, and similarly for the aqueous gel the difference on the same side is roughly double the above. This rise might be looked upon as an indication that these are true gels, since the velocity of the ions is retarded by them: added to this, the fact that the conductivity of the gel is four times as great as that of methyl alcohol shows that some portion of the salt must be ionised in the gel, though possibly some may be in the form of molecules.

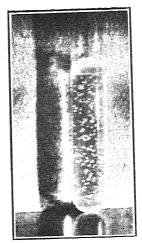
Hydrogen and hydroxyl ionic concentration was determined by adding a few drops of an alcoholic solution of a mixed universal indicator to the methyl alcoholic solution of calcium acetate, and then forming the gel with benzene. The resulting colour, deep greenish-yellow, indicated a  $p_{\rm H}$  of a little over 7, *i.e.*, slightly on the alkaline side, which agrees with the fact that acids destroy or inhibit the formation of the colloid. Previous controls were carried out in order to calibrate the colour changes, because Michaelis and Mizutani <sup>13</sup> have shown that rise in concentration of alcohol raises the  $p_{\rm H}$  and consequently the values to which the colours refer.

Low temperature experiments yielded the following results:—

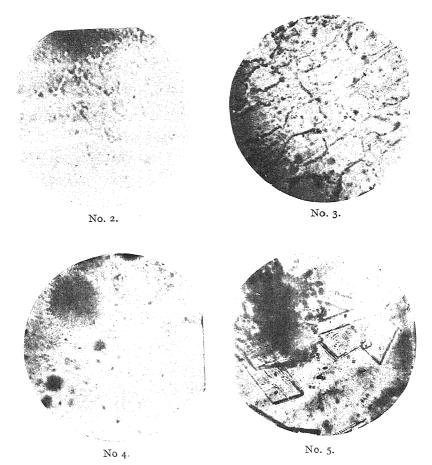
- Mixtures of ( $\alpha$ ) I volume of *iso*-propyl alcohol and I volume of benzene froze at  $-2^{\circ}$ .
  - (β) I volume of methyl alcohol and I volume of benzene froze at — 8°.
  - (γ) I volume of methyl alcohol and I volume of benzene with I volume of iso-propyl alcohol froze at — 10°.
  - ( $\delta$ ) The gel made as  $\gamma$  did not freeze at  $-16^{\circ}$ .
  - ( $\epsilon$ ) The gel made as  $\gamma$  with 5 per cent. more benzene froze at  $-12^{\circ}$ .
  - ( $\zeta$ ) The gel made as  $\gamma$  with 10 per cent. more benzene froze at  $-8^{\circ}$ .

No difference was noticed in the formation of the colloid on adding the mixed precipitants at 0° to the calcium acetate in methyl alcoholic solution at — 12°, but crystals of the salt formed more rapidly than at room temperature.

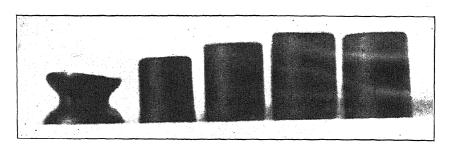
The fact that the benzene in the gel does not freeze at  $-16^{\circ}$  but does so in solution at  $-10^{\circ}$ , suggests that its physical condition is different in the two states, and from this it might be inferred that it either forms,



No. 1.



[To face page 1106.



A B C D E Fig. 16.—Drying of gelatin cylinders with increasing glycerin content.

[See page 1126.

with the calcium acetate, part of an ion or molecule loosely held together or, if it partly acts as dispersion medium, it cannot form crystals owing to the capillaries of the gel being so small as to prevent their formation, particularly under any pressure exerted by the gel itself. Parker 14 records that when liquids are in the pores of fine powders they have lower freezing-points than when they are in mass. The two phenomena may be analogous.

The Radii of the Capillaries.—The absorption and loss of water in silicic acid gels has been followed by means of the vapour pressure. Van Bemmelen 15 has carried out experiments which Zsigmondy and his co-workers 16 have extended, and they, as well as Anderson 17 have

calculated the size of the capillaries from the expression

$$r = \frac{2\sigma \rho_d}{p_s \rho_f \log p_s/p_w},$$

where r =capillary radius,

 $\sigma = \text{surface tension of water or other liquid,}$  $\rho_d$  = density of vapour of water or other liquid,

 $\rho_t =$  density of water or other liquid,

 $p_s$  = saturation pressure of gel at temperature of experiment,

 $p_w$  = vapour pressure of gel at the opacity point, i.e., where the intermicellar liquid evaporated from the capillaries.

To reduce to fundamental units the denominator of the fraction is multiplied by the density of mercury and by 981 dynes per cm. The values at 15° for a gel, made up with equal weights of a 0.553 per cent. solution of calcium acetate in methyl alcohol, iso-propyl alcohol and benzene, were  $\sigma=$  24.3 dynes per cm.;  $\rho_d=$  0.002474;  $\rho_f=$  0.8290 for the mixed liquids;  $p_s = 1.25$  cm. of mercury;  $p_w = 0.9$  cm. of mercury for the gel. Using Zsigmondy's apparatus for finding the ratio of  $p_s/p_w$ , from the average of numerous experiments the value for the capillary radii worked out to  $7.06 \times 10^{-7}$  mm.

The exact opacity point was somewhat uncertain, owing to crystal formation; but, as the liquid evaporated, a point was reached in each experiment where opacity appeared for some distance down into the gel: this never penetrated to the lower portions because the gel broke down at the surface with consequent evaporation of the liberated liquids.

Ultramicroscopic experiments were carried out by viewing films of the gel. The photographs show the same film in four stages of deterioration; No. 2 some of the micellæ as points of light; No. 3, the first signs of crystallisation; No. 4, a later stage: and finally through the ordinary microscope; No. 5, crystals of (CH<sub>3</sub>COO)<sub>2</sub>Ca. CH<sub>3</sub>OH after the gel had dried. In some films thin, straight threads were seen running right across the field of vision. It was found to be impossible to photograph them. Flade 5 and Freundlich and Dieselhorst 18 hold the view that such threads are very thin crystals.

In conclusion, the author wishes to thank Professor F. H. Newman for his kind criticism of the mathematical methods used.

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J. Amer. Chem. Soc., 43, 1011, 1921.
 Z. anorg. Chemie, 5, 466, 1894; 13, 233, 1897; 18, 14, 1898; 30, 265, 1902.
 Ibid., 71, 356, 1911; also Physik. Z., 14, 1098, 1913, et seq.
 Z. physik. Chemie, 88, 191, 1914.

# THE ELASTIC PROPERTIES OF GLYCERIN-GELATIN GELS AND OF GELATIN GELS HARDENED WITH FORMALDEHYDE.

By EMIL HATSCHEK.

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The Young's modulus of gelatin gels has until recently been determined directly on specimens in tension or calculated from the modulus of rigidity determined on specimens in torsion. The method most generally used for transmitting the stress to cylindrical or prismatic test pieces is to cast or fuse hard wood blocks to their ends, a procedure applicable only with gels which, like gelatin or cellulose acetate in benzyl alcohol, adhere to wood.

In a paper presented at the tenth Colloid Symposium at Ottawa <sup>1</sup> I have described a simple method of determining Young's modulus on specimens in compression and given a number of moduli, those of agar and silicic acid, as well as of gelatin hardened with formaldehyde, having been determined for the first time. The present paper shows the application of the method to a number of problems which have not so far received attention, partly owing to the inadequacy of the older methods,

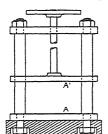


Fig. 1.—Press for loading cylindrical test pieces.

viz., the effects of ageing for several months and of cycles of temperature changes, the elastic anisotropy produced by permanent deformation, and the changes produced in isotropic and anisotropic gelatin gels by hardening with formaldehyde. Before these are described in detail it will be necessary to refer to some improvements in technique introduced since the first paper on the method was written and to discuss the limits of validity.

Cylindrical test pieces are loaded in the press shown in Fig. I, which is mounted on a common levelled base plate with the reading microscope. The sliding member of the press.

the guides of which are freely lubricated, weighs 321 gm.; the load can be increased by additional weights of 200 gm. each placed on the top disc. The faces A, A' are oiled with viscous paraffin to ensure that the ends of the test pieces slide freely.

Since it is impossible to cut gelatin gels so that really plane surfaces result it was necessary to devise a method of casting test pieces with plane ends. The procedure originally adopted is described in detail in the paper quoted; <sup>1</sup> it produces cylindrical test pieces with plane ends, the circular edge of which is rounded off by a meniscus. The pressure distribution is therefore not quite the same as it would be if the pressure were applied uniformly to the whole cross-section. The error is probably not great, and would be immaterial if the radius of the meniscus

were always the same; as it was, however, found to vary, e.g., with gels containing different percentages of glycerin, and to alter during hardening with formaldehyde, another method of casting test pieces was adopted which, while somewhat more elaborate, answers all theoretical requirements.

The moulds (Fig. 2) are again lengths of brass tubing to which are cemented base plates of plate glass, so that the axis of the tube is horizontal when placed on a levelled plate. The ends of the mould are closed by vaselined glass plates held in place by rubber bands. The mould is filled, through a hole in the middle of the length and on the end of the vertical diameter, to within about 5 mm. of the top, and an organic liquid run into the remaining space to prevent the formation of "fins" on the

finished test piece. After the standard period of setting one end plate is detached by slight tilting and twisting, and the test piece removed from the mould by pulling axially on the other glass plate. Specimens cast in this way have perfectly plane ends per-



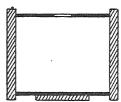


Fig. 2.—Latest type of mould.

pendicular to the axis; the cross-section is not a complete circle, and its area has to be found by calculation for each specimen.

For the calculation of Young's modulus it is essential to know the length of the cylindrical test piece when unstressed by any external load and by its own weight. At the time and temperature at which it is removed from the mould this length  $L_o$  may be taken to be that of the brass mould. The weight W and cross-sectional area A of the specimen having been determined, it is loaded in the apparatus described above with a load Q and the length  $L_q$  corresponding to this load read on the travelling microscope. It may be taken as established by previous work  $^2$  that the volume of gelatin gel remains constant under such stresses as used in the present investigation, so that the area of the specimen compressed to the length  $L_q$  is

$$A_q = AL_o/L_q$$

and the mean stress, taking into account the weight of the specimen, is

$$S = \frac{(Q + W/2)L_q}{AL_q}.$$

The deformation is  $(L_o - L_q)/L_o$ , and therefore the modulus E,

$$E = \frac{(Q + W/2)L_q}{A(L_o - L_o)}. \qquad . \qquad . \qquad . \qquad . \tag{I}$$

This formula has been used throughout, i.e., the true stress and the weight of the test piece have been taken into account.

The free length changes with the temperature and also appears to do so with age. Its direct measurement is difficult, as the specimens undergo some deformation in whatever position they are supported, and the most satisfactory way is therefore to measure the length of the test piece L when deformed by its own weight and to calculate the free length from this figure and the length  $L_a$  under the additional load Q.

<sup>&</sup>lt;sup>2</sup> R. Maurer, Wied. Ann., 28, 628, 1886; P. v. Bjerken, ibid., 43, 917, 1891.

When the weight of the test piece only acts on it, equation (I) becomes:

$$E = \frac{W/2 \cdot L}{A(L_o - L)},$$

therefore

$$\frac{(Q+W/2)L_q}{A(L_o-L_q)} = \frac{W/2 \cdot L}{A(L_o-L)},$$

which gives the value of  $L_{\nu}$ 

$$L_o = \frac{QLL_u}{(Q + W/2)L_q - W/2 \cdot L} \qquad . \qquad . \qquad (2)$$

This formula has been used throughout for calculating the free length of specimens except on the first occasion after they were taken from the mould. The calculated free length of such fresh specimens has also, in a few cases, been compared with the measured length, *i.e.*, the length of the mould, with excellent agreement.

The procedure adopted with gelatin gels having moduli of the order of some hundreds of gm. per cm.² is therefore as follows. The test piece is placed in the press, the top member of which is supported by a distance piece, and the length L determined. The test piece is then loaded with the top member (Q=321+W/2 gm.), and the length  $L_q$  read off. A further weight of 200 gm. is then placed on the pan, and the length  $L_q'$  corresponding to this load (Q'=521+W/2 gm.) noted. The whole operation can easily be carried out inside two minutes, a point to be emphasised in view of the high temperature coefficient of E and the absence of thermostatic arrangements. Before proceeding further, it seems desirable to produce evidence that (a) determinations on duplicate specimens show reasonable agreement, and (b) that E is a constant within the range of stresses used. With specimens of the usual size these stresses are about 28 and 43 gm./cm.² respectively for the external loads of 321 and 521 gm. The composition of the particular specimens to be quoted is immaterial to the present purpose.

Specimen.	A.	В.
Weight Cross Section $L$ $L_{\mathfrak{o}}$ (calc.)	93 13·31 5·83 5·87	88 gm. 12·96 cm.² 5·84 cm. 5·88 cm.
Q	321	521 gm.
Spec. A. $\begin{cases} L_q \\ \text{roo} L_q / L_o \end{cases}$	5·57 94·89 5 <sup>1</sup> 3	5·41 cm. 92·13 499 gm./cm. <sup>2</sup>
Spec. B. $\begin{cases} L_q & \text{roo} L_q / L_o \\ E & \end{cases}$	5*57 94*79 5 <sup>1</sup> 3	5.41 cm. 92.07 506 gm./cm. <sup>2</sup>

The values of E for the two stresses differ by less than 3 per cent. for specimen A and less than  $I \cdot 5$  per cent. for B; the agreement between the duplicates is equally satisfactory, and is obtainable only with specimens cast from the same sol and treated exactly alike from the moment of casting to that of determining the modulus. A set of three further

determinations may serve to show that even at much lower values the modulus is still sensibly constant over the same range of stresses.

Specimen.	C.	D.	Ε.
Weight . Cross-section	. 67 . 11.68	91 1 <b>3</b> .77	87 gm. 13.61 cm. <sup>2</sup>
$L_{o}$ (mould) .	. 5.66	5.87	5.95 cm.

These being fresh specimens, for which  $L_o$  was taken to be the length of the mould, L is not given in the following table:—

Q	321	521 gm.
Spec. C. $\begin{cases} L_q \\ \text{loo} L_q / L_o \\ E \end{cases}$	5·08 89·73 265	4·79 cm. 84·61 260 gm/cm. <sup>2</sup>
Spec. D. $\begin{cases} L_q \\ \text{ioo} L_q / L_o \\ E \end{cases}$	5·48 93·30 373	5·27 cm. 89·76 363 gm./cm. <sup>2</sup>
Spec. E. $\begin{cases} L_q & L_q/L_o \\ E & \end{cases}$	5·58 93·78 401	5·39 cm. 90·59 396 gm./cm. <sup>2</sup>

Even with these considerable deformations the modulus remains practically constant, the maximum difference between the values at the two stresses amounting to less than 3 per cent. (Spec. C). It will be seen that E for the higher stress is throughout smaller than for the lower, though the difference does not exceed what may reasonably be assumed to be experimental error. In the paper quoted above, I have shown that with higher stresses—up to 69 gm./cm.2—the decrease in the value of E becomes more marked and have pointed out that this is in agreement with, or supplements, Poole's results. On the assumption that the elastic properties of gelatin gel are those of a network of elastic fibrils orientated at random Poole deduced that the modulus of such a system must increase with increasing tensile stress and confirmed this deduction experimentally. The modulus of the system should, by extension of Poole's reasoning, decrease with increasing compression, and this appears to be borne out by my results.

Poole was also the first investigator to determine the modulus over a range of temperature, and to emphasise the necessity of doing so, in view of the high value of the temperature coefficient—about 5 per cent. per degree for 12 per cent. gels over the range from  $5.7^{\circ}$  to  $18^{\circ}$ . Much of the earlier work still quoted in the textbooks was carried out without temperature control, and the authors do not even mention the temperatures at which E was determined; an omission that may account for some discrepancies, though others, regarding, e.g., the effect of glycerin on the modulus, are not easy to explain on these grounds alone.

Poole carried out his measurements (in tension) in a thermostat, the liquid being a mixture of benzene and carbon tetrachloride of suitable density so as to eliminate the weight of the test pieces. While this is undoubtedly the ideal arrangement, it appeared too complicated with my method which, anyhow, did not call for the elimination of the weights.

<sup>&</sup>lt;sup>3</sup> H. J. Poole, Trans. Faraday Soc., 21, Part I., 114, 1925.

The problem of getting the specimens to a given temperature proved to be bound up with that of preserving them for long periods while protecting them from changes in the water content, attack by organisms and deformation by their own weight. Loss or gain of water can be prevented by keeping the test pieces in an air-tight vessel with little excess volume, provided they all have the same composition; if watergelatin gels of different gelatin content, or water-glycerin gels with different glycerin concentrations, are kept together, transfer of water from the less to the more concentrated gels begins at once and, especially with the glycerin gels, proceeds rapidly. In practice, specimens were therefore kept singly in air-tight tins or small glass jars, which must have plane bottoms, to avoid distortion of the end faces of the specimens by their own weight as any such distortion, and especially any deviation from parallelism, renders the test pieces useless for further measurements. Gelatin-water gels can be preserved during this storage by the addition to the water of O·I per cent. of mercuric chloride, which has no measurable effect on the modulus; gels made with glycerin-water keep perfectly if the glycerin content of the mixture is over 40 per cent.

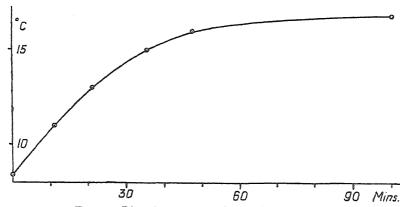


Fig. 3.—Rise of temperature in standard test piece.

While this procedure was reasonably satisfactory as a method of storage, warming a number of small air-tight receptacles in the thermostat proved inconvenient and uncertain. The method finally adopted was to keep the specimens under mineral oil in large stoppered jars. A neutral lubricating oil of sp. gr. 0.894 was used, in which the weight of the test pieces is reduced to a little more than one-tenth, so that no deformation occurs; specimens of different composition can be kept together for weeks without showing any change of weight, and oil bath and specimens can be conveniently brought to the desired temperature. As it is, of course, impossible to ascertain the temperature of a specimen, it appeared necessary to determine, at least approximately, the rate of heat transfer into a test piece of the usual size.

For this purpose a cylinder 32 mm. diameter  $\times$  55 mm. long was cast round a thermometer with small bulb (about 0.2 c.c.), allowed to set and age 24 hours, and then placed in an oil bath at 8.4° until the mercury was stationary. It was then immersed in an oil bath at 16.8° and the times, at which the thermometer read II.0, I3.0, I5.0, I6.0, I6.5 and I6.8° respectively, taken by means of two stop watches alternately started and stopped together. The result is plotted in Fig. 3. The

interval covered is that in which the majority of measurements was carried out, but several other curves were taken which agree well with that shown. The rapid—and apparently immediate—rise of temperature at the centre of the cylinder seems to indicate that the transfer of heat is not due exclusively to conduction. Whether anything like convection is possible and occurs in gelatin gel will have to be the object of special experiments; for the present investigation it was necessary to know only after what time test pieces of gel could be assumed to be at the temperature of the surrounding oil bath. In practice, they were always given at least four hours, but more frequently left in the thermostat overnight.

The temperature of the room in which the measuring apparatus was mounted as a rule differed only by three or four degrees from that of the oil bath. Specimens were taken out singly, wiped rapidly with muslin and placed in the press; the three lengths L,  $L_q$  and  $L_q'$  were then read, the whole operation being easily completed within two minutes. While there is some uncertainty about the temperature of the test piece, it is fairly certain that a series of three or four test pieces measured consecutively were all at the same temperature, which is the point of chief importance in most of the work to be described.

The first subject in need of investigation appeared to be gelatin gels containing glycerin, since they offer certain advantages for experiments on permanent deformation. The previous history of this subject is short but curious. Gels containing glycerin were investigated for the first time by E. Fraas,  $^4$  who reached the conclusion that the modulus was determined by the gelatin concentration alone, and was not altered by the addition of even high percentages of glycerin to the dispersion medium. E. Leick,  $^5$  ten years later, found that the modulus, at constant gelatin concentration, was increased considerably by the addition of glycerin, and gave the following figures for gelatin gels containing 20·9 gm. of gelatin in 100 gm.; c is the number of c.c. of glycerin in 100 c.c. and E Young's modulus in gm./cm. $^2$ :

Fraas worked with almost the same gelatin concentration—20 per cent.—and neither author states the temperature at which the measurements were made. Both added the stated proportions of glycerin to gelatin sols made up at suitable—and therefore different—concentrations, which introduces complication; the methods adopted for preparing the aqueous sols, such as boiling gelatin not previously allowed to swell with water were not in accordance with modern colloid practice.

The question how sols with the same gelatin content but different glycerin concentrations should be prepared with due regard to the uniformity of procedure essential in all investigations on the properties of gels is not quite simple. On the whole, the most reasonable procedure seemed to be the following: equal weights of gelatin were allowed to swell to saturation in equal volumes of the various glycerin-water mixtures and were then dispersed in the water bath at the same temperature. This ensures at least that all the test pieces up to the moment of casting have the same "thermal history." The actual procedure was as follows:

<sup>&</sup>lt;sup>4</sup> E. Fraas, Wied. Ann., **53**, 1074, 1894. <sup>5</sup> E. Leick, Drude's Ann., **14**, 139, 1904.

The concentration in gelatin throughout this paper is gm. of gelatin/c.c. of dispersion medium, i.e., a 10 per cent. gel is one made up from 10 gm. of gelatin in 100 c.c. of water or glycerin-water mixture. As each test piece was cast from a separate batch of sol, 80 c.c. of dispersion medium was measured into a 140 c.c. beaker, the whole weighed and then 8 gm. of gelatin for a 10 per cent. gel weighed in and the total weight noted. The gelatin was then allowed to swell at room temperature until, as far as could be judged by inspection, the process had become stationary. The time required for this increases considerably with increasing glycerin concentration, and amounts to at least 48 hours for 50 per cent. (by volume) glycerin-water mixtures. All preparations in the same series were, however, allowed to swell or soak for the same time, i.e., that required by the mixture richest in glycerin, and were then

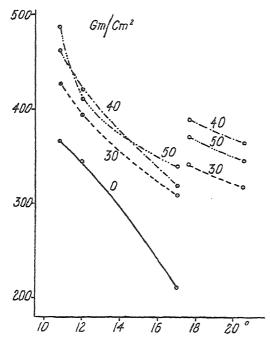


Fig. 4.—Temperature-modulus curves of gels containing 0, 30, 40 and 50 per cent. of cane sugar.

placed in the water bath at 50°. When dispersion and escape of air were complete, each beaker was placed on the balance and loss of weight made up by adding water at about 50°, after which operation the beaker was replaced in the water bath for a few minutes. One test piece was then from each batch and allowed to set in the mould for at least 24 hours before removal, after which it was generally kept in the oil bath for another 24 hours before the first measurements were made.

Leick had also used cane sugar as addition, and found that it raised the modulus. It seemed desirable to re-investigate the behaviour of

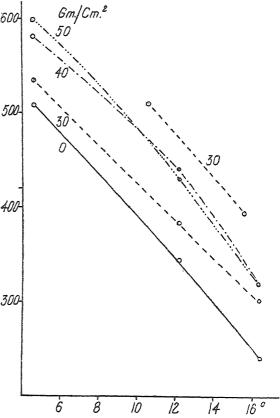
such gels as well as of those containing glycerin, and a number of them were prepared, the dispersion medium being cane sugar solutions containing respectively, 30, 40 and 50 gm. of sugar in 100 c.c. of solution. In other respects the procedure was exactly the same as that adopted with the glycerin-water mixtures.

Numerous series of determinations with either addition were carried out, over temperature ranges lying between the extremes of 0° and 21.5°. The results are confusing, but agree in so far that they are irreconcilable with either Fraas's or Leick's findings. The addition of either sugar or glycerin raises the modulus at all temperatures and ages, compared with aqueous gels of the same gelatin content, but the modulus does not increase with increasing glycerin (or sugar) concentration as simply and continuously as found by Leick.

A very few examples only can be given here, which can be interpreted in the light of subsequent investigation on the effect of age, to be given in detail below. Fig. 4 shows the  $E-\theta$  curves of gelatin gels all containing 10 gm. of gelatin in 100 c.c. dispersion medium containing respectively 0, 30, 40 and 50 gm. of sugar in 100 c.c. The measurements at  $17.0^{\circ}$ ,  $12.0^{\circ}$  and  $10.8^{\circ}$  were carried out in that order, 48, 107 and 193 hours after removal from the moulds. Even the lowest sugar concentration raises the modulus perceptibly, but the curves for 30, 40 and 50 per cent. lie close together and, what is even more striking, for a small range of temperature the modulus of the 50 per cent. gel is lower than

that of the 40 per cent. one. The differences do not much exceed the experimental error, but they occur in all the series investigated.

Measurements were taken after 221 hours at 17.6° and after 248 hours at 21.0°. It will be seen that the moduli of all four gels at 17.6° are now higher the values found at the lower temperature of 17.0° 173 hours before. This shows that in the interval a further ageing of the gel, with an increase in the modulus, must have taken place; the order in which measurements happened to have been made makes this change clearer than it is in some shows



of the other series. Fig. 5.—Temperature-modulus curves of gels containing Fig. 5 shows a o, 30, 40 and 50 per cent. of cane sugar.

second set of determinations on gels containing the same sugar concentrations as in the previous set; the readings were taken at the following times after removal from the mould:  $4.6^{\circ}$  48 hours,  $16.4^{\circ}$  80 hours, and  $12.2^{\circ}$  96 hours. Two further readings were then taken, at  $15.6^{\circ}$  after 125 hours and at  $10.6^{\circ}$  after 167 hours. All the lines connecting these pairs of readings lie above the earlier curves in the same interval; only that for 30 per cent. of sugar is shown, so as not to confuse the figure too much.

Gels containing glycerin behave very much like those just described. Fig. 6 shows the E- $\theta$  curves for gels with respectively 30, 40 and 50 per

cent. of glycerine in the dispersion medium. The curves intersect once, but for the greater part of the range the 50 per cent. gel has a modulus lower than those containing less glycerin. Fig. 7 finally shows the curves for two gels only, with 33 and 50 per cent. glycerin, which bear a striking resemblance to the curves shown in Fig. 4. The first three readings, at 15.4, 10.8 and 4.1° were taken 48, 79 and 96 hours after removal from the moulds. The curve for 50 per cent. intersects that for 33 per cent. twice in that interval. The remaining two readings were taken 107 and 123 hours after removal, and closely resemble the last two readings in Fig. 4: the values at 17.4° are higher than the previous ones at 15.6, and the curve of the 33 per cent. specimen lies entirely above that of the 50 per cent. one.

The unavoidable conclusion to be drawn from all this evidence—

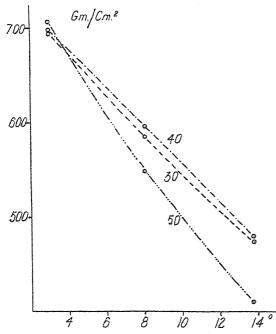


Fig. 6.—Temperature-modulus curves of gels containing 30, 40 and 50 per cent. of glycerin.

which represents fraction only of the experimental material —is that the modulus of the gels so far described keeps increasing for a very considerable time. The rate of increase appears to depend not only on glycerin or sugar concentration, but also very probably on the temperature through which the gel has been taken, so that the whole phenomenon becomes extremely complicated, and its exhaustive investigation laborious. Pending this, it seemed at least desirable to take measurements at intervals over even longer periods and to

ascertain if and when the modulus reached a constant value. For this purpose a number of specimens were cast with all possible precautions, weighed and kept under lubricating oil in glass jars with ground stoppers, which were placed in the thermostat or a large water bath. The weight of the specimens was checked after every determination of the modulus and remained constant over the whole period.

The figures for two specimens are given below; both contained 12 gm. of air dry gelatin in 100 c.c. of dispersion medium, which was 33 per cent. glycerin for  $G_{33}$  and 50 per cent. for  $G_{50}$ .

Time (days)	2	6	39	54	60
Temperature	17.0	12.2	14.4	15.0	16.5
$E \stackrel{G_{33}}{\sim} \cdot \cdot \cdot$	398	569	575	623	653
$^{2}G_{50}$	368	505	547	558	566

Both moduli accordingly increased by about 50 per cent. in the course of two months and in the particular thermal conditions. A number of other specimens gave similar results, *i.e.*, a slow increase over two months and more. The effect of keeping the test pieces at low temperature is shown—though not conclusively—by the following experiment: test pieces of the same composition as those given above were cast, and the modulus found to be 383 gm./cm.² at 13.0° 48 hours after casting. They were then kept in cold storage (in airtight tins) at 3-4° for seven days, at room temperature for three days, and finally measured at 13.2°, when the modulus was found to be 527 gm./cm.²

It is clear that the results described so far establish two points only:

glycerin (and cane sugar) to the extent of 30 or more per cent. of the dispersion medium raises the modulus above that of aqueous gels, and that the modulus keeps increasing with age for a period of two months, and possibly for longer. To get a clearer insight into the ageing process it will be necessary to proceed somewhat as follows: the test pieces are kept at a constant temperature and the modulus determined at intervals at that temperature, untilever—it becomes constant; they are then

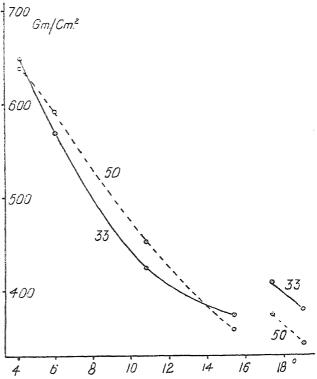


Fig. 7.—Temperature-modulus curves of gels containing 33 and 50 per cent. of glycerin.

kept at another, higher constant temperature and the modulus again determined at intervals to ascertain whether the effect of ageing at the lower temperature is partly reversed at the higher temperature, a behaviour which would be analogous to the change in viscosity of sols aged at a low temperature and subsequently warmed to a higher one. Only after some such investigation will it be possible to decide what method of comparison between gels containing different concentrations of sugar or glycerin has a simple physical meaning. The effect of the glycerin concentration on the rate of permanent deformation, however, as will be seen from the next section of this paper, is as simple as the connexion between the glycerin content and Young's modulus is ambiguous at present.

#### Permanent Deformation.

It is known that continued application of even moderate stresses leads to the irreversible deformation of gelatin gels, and it is likewise known that, conversely, the stress necessary to maintain a given deformation decreases with time. The investigation to be described has been directed to answering a question which so far does not appear to have been put: what fraction of a deformation which is maintained constant becomes irreversible with time? The experimental procedure was as follows: cylindrical specimens were cast and aged in the usual way, and their free length  $L_o$  measured. They were then compressed to a known fraction, generally 90 per cent., of this length in small presses (Fig. 8) and kept under oil in stoppered jars. They were released from time to time, the length  $L_t$  after the time T from the application of stress

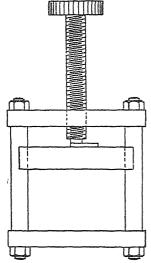


Fig. 8.—Press for deforming specimens permanently.

measured after it had become constant, and then recompressed to the same length as before, viz., 0.9L<sub>q</sub>.

The results for three gels, all containing 12 per cent. of gelatin in 100 c.c. of 30, 40 and 50 per cent. glycerin-water mixtures, are shown in Fig. 9. The ordinates on the left-hand scale give the lengths of the specimens in per cent. of the original length against the times of release as abscissæ (hours); the figures on the right-hand of the diagram give the ordinates, *i.e.*, the fraction of the deformation which is still reversible, in per cent. of the total constant deformation. The fraction of the deformation which has become irreversible is accordingly 100 - y.

The effect of increasing glycerin concentration shows itself very markedly in increasing the time required for a given percentage of the deformation to become irreversible. The following table shows the times—taken from the graph— $T_{30}$ ,  $T_{40}$ , and

 $T_{50}$  required by the three gels with the glycerin concentrations given by the indices to reach the same values of y:

<i>y</i> .	T <sub>a0</sub> .	$T_{40}$ .	$T_{50}$
70	7.5	9.5	14.0
60	14.0	17.0	25.0
50	25.0	31.5	47.0
40	50·0	61.0	132.0

The ratios of the times of equal deformation are approximately constant:

y =	70.	60.	50.	40.
$T_{40}/T_{30}$	1.40	1.21	1.26	I:22
$   \begin{array}{c}       y = \\       T_{40}/T_{30} \\       T_{50}/T_{30} \\       T_{50}/T_{40}   \end{array} $	1.86	1.78	r·88	2.60
$T_{50}/T_{40}$	1.47	1.47	T•40	2.76

The two extreme values involving  $T_{50}$  diverge considerably, but the curve in that region is somewhat irregular, probably because the speci-

mens were not kept at constant temperature during the whole period of investigation. For this reason, although the room temperature varied only from 15.0 to 17.7° at the time of the measurements, it seems useless to enquire at this stage whether there is a simple connexion between the time ratios and the viscosities of the dispersion media.

Various ways of representing the time-deformation curves have been tried; the following equation fits reasonably well between T= 20 and T= 240:

$$D - y = K \log T,$$

where D is the constant deformation and K a constant. If y is expressed in per cent., D = 100, and for logs to the base 10 the constants are:

$$K_{30} = 33.5$$
 to 37.6  $K_{40} = 29.8$  to 31.7  $K_{50} = 27.6$  to 28.5.

At constant temperature the constancy of K would presumably be more satisfactory.

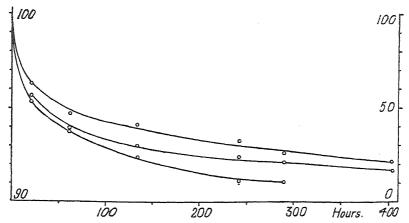


Fig. 9.—Time-deformation curves of gels containing 30, 40 and 50 per cent.

of glycerin.

Ordinates: left, length of recovered specimen in per cent. of original free length; right, per cent. of impressed deformation.

The stress which, on continued application, produces these deformations is quite moderate: since the average value of the modulus may be taken to be about 450 gm./cm.<sup>2</sup> and the permanent deformation applied was 10 per cent., the initial stress is of the order of 45 gm./cm.<sup>2</sup> It has been shown by Rankine <sup>6</sup> that the stress required to maintain a constant deformation decreases without becoming zero, and this relation has not been studied in the present investigation. Another question, however, appeared to be of interest: do gelatin gels become elastically anisotropic by permanent deformation? It is known that they become optically anisotropic, and I have shown <sup>7</sup> that the accidental birefringence remains practically constant while the stress decreases. I have also shown by the air bubble method <sup>8</sup> that in a permanently compressed gel the tensile strength is a minimum in the direction of compression. This method does no more than show the existence and direction of a

<sup>&</sup>lt;sup>7</sup> E. Hatschek, General Disc., Faraday and Physical Socs., 1920; Appendix to Trans. Far. Soc., 16.

<sup>8</sup> E. Hatschek, Koll.-Zeitschr., 49, 244, 1929.

minimum of tensile strength, but gives no information regarding the

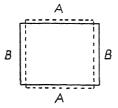


Fig. 10.—Permanent deformation of square prism.

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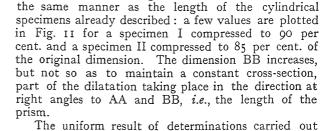
divergence between this minimum and the maximum in the directions of dilatation.

The determination of the moduli in two directions at right angles, one being the direction of compression and the other the direction of dilatation, was carried out as follows. Square prisms of gelatin gel were cast in brass moulds about 30 mm. square inside and allowed to age for the usual time; they were then cut into lengths of about 40 mm., this course being permissible as the cut faces remain free. The side of the square of the free specimen was then

measured and its modulus determined in the usual way, the stress being calculated from the initial dimensions, and the same allowances made for cross-section and the own weight of the test piece as with the cylindrical specimens.

The prism was then compressed in the press illustrated in Fig. 8 in the direction of one side of the square to a known fraction of the original height, so that the cross-section became rectangular (Fig. 10).

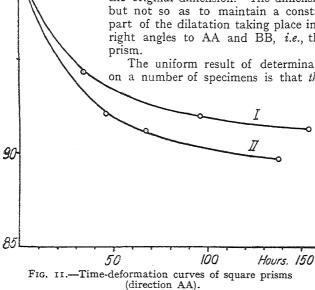
From time to time the test pieces were removed from the press, and the moduli measured both in the direction of compression AA and in the direction of dilatation BB. The height AA decreases with time in



on a number of specimens is that the modulus in the

direction compression remains sensibly constant, and that at angles to it increases. Two examples out of many will be sufficient:

Prism N<sub>12</sub>, 12 gm. gelatin in 100 c.c. of water, after 140 hours' compression to 85 per cent.



original height, temperature 16.8°.

 $E_{\rm AA} = 293 \ {\rm gm./cm.^2}.$  $E_{\rm BB} = 343 \ {\rm gm./cm.^2}.$  Prism  $N_{12}$   $G_{50}$ , 12 gm. gelatin in 100 c.c. of 50 per cent. glycerin, after 155 hours' compression to 90 per cent. of original height, temperature 16.8°,

$$E_{\rm AA} = 344 \text{ gm./cm.}^2$$
.  $E_{\rm BB} = 439 \text{ gm./cm.}^2$ 

No attempt has so far been made to co-ordinate the ratio of the two moduli with the degree and duration of deformation, as such an investigation will also have to be carried out at constant temperature. The fact established by the present series of measurements, that the modulus in the direction of dilatation is greater than that in the direction of compression is in qualitative agreement with the demonstration furnished by the air bubble method, that the tensile strength is greater in the direction of dilatation than in that of compression. Both results must obviously be taken into consideration in all theories of gel structure, but their implications will be more conveniently discussed after the effects of hardening with formaldehyde have been described.

# Gelatin Gel Hardened with Formaldehyde.

In my first paper on this subject I have given one graph illustrating the increase in the modulus during hardening with formaldehyde for two gels with different gelatin concentrations. This is apparently the first investigation on the subject, if for no other reason because it is impossible to determine this modulus on specimens in tension, since during the progress of hardening gelatin detaches itself from any support—wood or glass—to which it adheres in its original state. The specimens referred to above were hardened in vapour, but in the present series they were placed into known volumes of formaldehyde solution of known concentration.

Fig. 12 illustrates the change in the modulus with the time of immersion for two specimens of the same size, about 58 mm. long  $\times$  42 mm. diameter originally, A containing 12 gm. and B 15 gm. of gelatin to 100 c.c. of water, each immersed in one litre of 2 per cent. formaldehyde solution. The specimens were taken out from time to time, dried and weighed, and the modulus then determined in the usual way. As the specimens shrink it was also necessary to re-determine the radius and re-calculate the stress at every determination; the load had to be increased gradually to 921 gm. (corresponding to a stress of about 73 gm./cm.²). Even with this the deformation towards the end amounted to less than I per cent., so that the error in the highest values of E may amount to IO per cent.

A steep initial increase is followed by a much slower continuous rise which, in the last stage, may not be much greater than the experimental error. The times, however, at which dE/dt begins to decrease markedly, viz., about 200 hours for the 15 per cent., and 260 hours for the 12 per cent. gel, seem extremely high when it is considered that the rate of hardening is controlled by the rate of diffusion of a substance with the low molecular weight of 30, and that the total path is equal to the cylinder radius, 21 mm. Conditions are somewhat complicated by the diffusion taking place not only through the cylindrical surface, but also through the plane ends, which it is not possible to seal; fused-on glass plates, which do so effectively in most salt solutions, invariably detach themselves in formaldehyde. It is, however, possible, with a few permissible simplifications, to deduce an ideal time-modulus curve as follows:

The moduli measured and plotted in Fig. 12 are the ratios: stress/deformation for test pieces which have not a uniform modulus over their entire cross-section, but may in first approximation be considered as consisting of an outer cylindrical tube of completely hardened gelatin

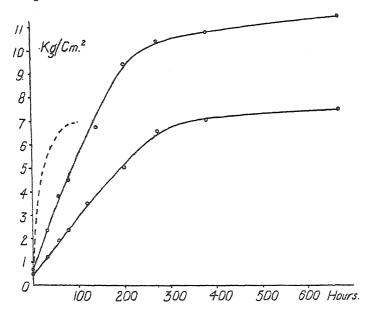


Fig. 12.—Time-modulus curves of gels hardening in formaldehyde (I, 12 per cent.; II, 15 per cent. gelatin; III, ideal).

and a cylindrical core of original gelatin. If we call R the radius of the specimen, r the internal radius of the tube (or external radius of the core),  $E_t$  the initial modulus,  $E_f$  the final modulus (when fully hardened), and  $E_a$  the average modulus determined from time to time, we have:

$$\pi[r^2E_i + (R^2 - r^2)E_f] = \pi R^2E_a,$$

whence

$$E_a = r^2/R^2(E_i - E_f) + E_f. (3)$$

If r can now be expressed as a function of time, we obtain the apparent or average modulus  $E_a$  as a function of time.

In the case under consideration, the solute which diffuses in (formaldehyde) reacts with the substance of the gel itself, and the circle with the radius r is, ex hypothesi, the boundary of the zone in which this reaction has completed itself. The case is therefore analogous with that in which the incoming solute reacts with one present in the gel to form a precipitate. The law according to which the boundary of the zone of precipitate advances when diffusion takes place parallel to the axis of a cylindrical column of gel has been deduced analytically and verified experimentally. Diffusion into the cylindrical surface has apparently

<sup>9</sup> A. Winkelmann, Handb. d. physik., Vol. I., 1459, 1908, where also literature; H. W. Morse and G. W. Pierce, Z. physik. Chem., 45, 589, 1903.

not been investigated so far, although the analogous problem of heat conduction in a cylinder is familiar. It appeared desirable to obtain some idea, not only of the function, but of the constants, and the following experiment was accordingly carried out in duplicate:

Cylinders of the standard size were cast from a sol containing 12 gm. of gelatin in 100 c.c. of a I per cent. solution of lead acetate. Glass plates were fused to the plane ends and the specimens submerged in about 500 c.c. of saturated solution (about 3M) of potassium chromate. As this diffuses in, lead chromate is precipitated, the edge of the precipitation zone being exceedingly sharp, so that its radius—r in the symbols measured used—can be with great accuracy. In Fig. 13 R-r is plotted in mm. against the time in

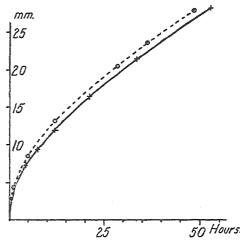


Fig. 13.—Diffusion into cylindrical surface.

hours, for two specimens prepared one after the other, so that the very slight difference between them is probably due to a difference in temperature.

The distance of the boundary from the periphery is very accurately represented as a function of time by the equation

$$R - r = K \sqrt{t}$$
.

By introducing this value in equation (3) we obtain  $\boldsymbol{E_a}$  as a function of time:

$$E_a = \frac{(R - K\sqrt{t})^2}{R^2} (E_i - E_f) + E_f \quad . \tag{4}$$

It is of interest to test this formula on experimental values.  $E_i = 300$ and  $E_f = 7000$  are, in round figures, the moduli of the 12 per cent. gel in Fig. 12. As regards K the choice is a little more difficult, but for the chromate precipitation (Fig. 13) K = 3.9 for t in hours and r in mm. The diffusing solute,  $K_2CrO_4$  has the molecular weight 194.75, whereas that of formaldehyde is 30, but very little chromate is used up or, in other words, the boundary of the precipitate is practically where the diffusion boundary would be if no precipitation were taking place. We may allow for the latter factor by assuming for K a value of say 2, in spite of the much lower molecular weight of formaldehyde, and the dotted line in Fig. 13 shows the curve for  $E_a$  calculated from this and the previously assumed values. If this is compared with the experimental curve for the 12 per cent. gel, and if it is borne in mind that diffusion into the specimens takes place into the ends as well as into the cylindrical surface, so that hardening should caeteris paribus proceed more rapidly than in the ideal case, the conclusion becomes inevitable that considerable quantities of formaldehyde are removed from the solution as it diffuses in and that, possibly, diffusion is retarded by the process of hardening itself, i.e., that the hardened gel obstructs diffusion more than the

original one.

A detailed examination of the first point would go much beyond the scope of the present paper. For the present it is sufficient to say, that the formaldehyde concentration in the outside liquid has been determined for several sets of specimens from time to time. When it has become constant an amount of formaldehyde has been taken up by the gel which is more than double the amount that would be required if the total nitrogen in the gel were present as NH<sub>2</sub> and each molecule combined with one of CH<sub>2</sub>O. The most probable explanation is condensation of the latter, but this will require a good deal of further investigation.

The diffusion velocity for a given solute in natural and hardened gel was compared in the following way: two cylinders about 24 mm. diameter were cast from a sol containing 12 gm. of gelatin in 100 c.c. of 0.5 per cent. lead acetate solution. One of these was then hardened in 10 per cent. formaldehyde solution containing 0.5 per cent. of Pb acetate, so as to leave the concentration of the salt unaltered in the gel. Concentrated potassium chromate was then allowed to diffuse axially into both cylinders, and the distance D of the precipitation boundary from the end was measured after a time. The results were:

		# (ho	urs).	D (mm.).
Original gel		. 31.	.5	27
Hardened,,	•	• 59		23

The function connecting t and D is known to be (loc. cit.<sup>9</sup>):

$$D=K\sqrt{t},$$

and the values of K are

Original. Hardened. 
$$K = .$$
 4.81 2.99

The diffusion velocity in the hardened gel is therefore considerably lower than that in the original one, and this also means a lowering of K

in equation (4).

The results illustrated in Fig. 12 are typical of a number of others, apart from small irregularities, and no further examples are necessary. It seemed, however, of great interest to examine the behaviour of anisotropic gels when hardened by formaldehyde, and the two permanently deformed prisms  $N_{12}$  and  $N_{12}G_{50}$  were used for the purpose.  $N_{12}$  was hardened in 5 per cent. formaldehyde solution, and  $N_{12}G_{50}$  in a mixture of equal parts of 10 per cent. formaldehyde solution and of glycerin; this had the effect of keeping the formaldehyde concentration equal for both specimens and of preventing diffusion of glycerin out of  $N_{12}G_{50}$ . Fig. 14 shows the increase in the moduli with time; in both gels the moduli in the direction AA and BB grow as if they were the moduli of two gels of different gelatin concentrations.

The curves for  $N_{12}$  bear a general resemblance to those for the gelatin cylinders in Fig. 12. Whether the small fall in the value of both E between the last reading but one and the final reading has any significance or lies within the limit of experimental error is difficult to say, but the other differences between the curve for the prism  $N_{12}$  and the cylinder are accounted for by the peculiarities of diffusion into any polyhedral mass of gel. If we consider a cross-section remote from the ends the diffusion boundary does not remain a rectangle, but its corners

become more and more rounded, and conditions still more complicated prevail at the eight trihedral angles at the end faces. The latter also undergo some distortion which makes the calculation of the loaded cross-section somewhat uncertain; for this reason, and also on account of damage to the edges readings were discontinued, although probably the moduli had not reached their maximum value.

The moduli of the gel containing 50 per cent. glycerin not only reach a much lower value in the same time, but the increase is practically linear. The lower rate of increase is, at any rate in part, explained by the lowering of the rate of diffusion caused by the much increased

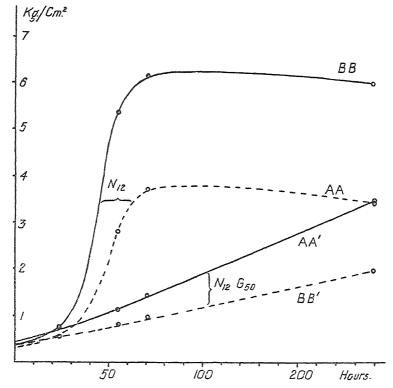


Fig. 14.—Time-modulus curves of deformed prisms hardening in formaldehyde.

viscosity of the liquid phase of the gel, but this alone does not account for the simple shape of the E-t curve. There is, however, an interesting piece of evidence that the presence of glycerin in gelatin gels not only retards diffusion but somehow also "smoothes out" the very characteristic effects caused by the presence of edges on the bodies of gel into, or out of, which diffusion takes place. One of the best known of these effects is the change of shape which, e.g., cylinders undergo on drying. A cylinder of 10 to 15 per cent. gel on drying first assumes the shape of a barrel with convex ends and finally (if not very long) that of a single shell hyperboloid with concave ends. The two stages are

shown diagrammatically in Fig. 15, and a photograph of the final stage of a typical specimen is given at A in Fig. 16. These phenomena are

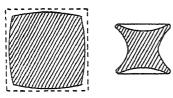


Fig. 15.—Successive stages in drying of (aqueous) gel cylinder.

controlled by the geometry of the body of gel, and it would seem reasonable to assume that the rate of diffusion of water to and through the surface enters merely as a constant or, in other words, that gels containing glycerin should, though more slowly, undergo similar changes during corresponding stages of the drying process. This, however, is

not the case, as shown by the specimens B to E in Fig. 16, showing cylinders all originally of the same size and gelatin content, with the following dispersion media: B 30, C 40, D 50 and E 60 per cent. of glycerin. B is in the stage in which a gelatin-water specimen would have all concave faces, while E would have convex ones, but all four specimens show practically no deviation from the cylindrical shape. The final shapes can, of course, not be expected to be even approximately the same as those of aqueous gels, which dry down to a water content of about 16 per cent., but the comparison as made above is quite fair.

There may be no connection between the effects just described and the "smoothing" of the E-t curves, but it is a striking fact that in two processes which are controlled by diffusion the presence of glycerin has an effect beyond that of retarding the processes uniformly.

#### Discussion of Results.

In the following it is proposed to examine how the experimental results so far described, many of which are new, bear on the most generally accepted theory of the structure of gelatin gels, that which assumes them to be "two-phase (solid-liquid) bodies—where the solid phase has the form of a mesh of cylindrical fibrils or threads." Poole, from whom this description is quoted, has done a great deal to provide support for the theory by showing that the elastic behaviour of such a structure, as deduced mathematically, is in good agreement with the elastic properties of gelatin gels determined experimentally.

The first thing calling for an explanation in terms of this theory is the effect of the addition of glycerin. As far as the evidence goes at present, glycerin raises the modulus, but over a certain range of temperature and, probably, age, increasing the glycerin concentration beyond about 40 per cent. causes no further increase of E. An investigation on the velocity of diffusion in gels containing glycerin published by me some time  $^{11}$  ago seems to throw light on the elastic behaviour. It is shown there that, if gels containing the same amount of gelatin but different concentrations of glycerin are assumed to contain the same amount of "solid" phase, and if the same reactant is allowed to diffuse axially into cylinders of the different gels, the following relation should hold for the distances  $D_1$ ,  $D_2$  of the reaction boundaries from the origin:

$$D_1/D_2 = \sqrt{\eta_2/\eta_1}.$$

The formula represents the experimental results within a few per cent., but with increasing glycerin content, i.e., increasing  $\eta$ , the distances D become increasingly greater than the calculated values. This difference is ascribed to dehydration of the "solid" phase, which produces two effects: reduced volume of the filaments, and therefore increased liquid cross-section available for diffusion on the one hand, and slight lowering of the viscosity of the glycerin-water mixture, both of which effects tend to assist diffusion.

If dehydration of the fibrillar structure could be shown to raise the modulus, the results of the diffusion experiments would be in good agreement with the general finding that moderate glycerin concentrations produce this effect. Any explanation involving hydration must, in the absence of any direct method of determination, rest on inference, and the whole position has been stated so clearly and completely by Poole (loc. cit., 3 p. 131) for aqueous gels that the simplest way of summarising it is to quote him verbatim: "Two satisfactory explanations of the foregoing data can, however, be postulated. The first is that the solid phase in gelatin jellies is capable of a reversible hydrolysis which results in products soluble in the liquid phase, the effect being roughly governed by massaction conditions.

"The second suggests that practically no solution of the solid phase takes place, but that the observed elasticity changes are changes in the elasticity of the solid phase itself on account of hydration. Two cases arise here: (a) either the hydration is greater at higher temperature and the elasticity diminishes with hydration, or (b) the hydration becomes less with rising temperature and the elasticity increases with increasing hydration, the water molecules acting as bonds between the protein molecules."

After remarking that both explanations fit the facts considered by him so far, Poole continues: "In this connection two experiments are of an almost crucial nature.

"In determining the elasticity of dry gelatin, it was observed that the values obtained increased from a mean of  $2 \cdot I \times 10^{10}$  C.G.S. units to  $3 \cdot I \times 10^{10}$  C.G.S. units in the final drying from about 15 per cent. of water to zero. This seems strong evidence against the possibility that the water molecules are the binding links giving rise to the elasticity of the solid phase. We are then left with the alternatives of a structure which varies in size as a result of a reversible reaction effect and an insoluble structure whose elasticity is determined by its degree of hydration, being less the greater the hydration. The following observation is considered, however, to be capable of affording a decision.

"In the course of a series of experiments . . . on the variation of elasticity of gelatin jellies with temperature, it was found that at the highest temperature employed the elasticity was so small that the hydrostatic forces were insufficient to maintain the cylinders in a vertical position, and the weight of the wire then caused them to droop over in the liquid. While in this position they were brought to a lower temperature. Instead of the original shape being restored on cooling, as would be expected if the structure were built up of material whose elasticity only were variable with temperature, the deformed shape was maintained, but the elasticity returned to a value appropriate to the lower temperature. . . . It seems probable, therefore, that the elasticity of gelatin jellies varies with temperature because of changes in the equilibrium constant of a reversible reaction either of hydration or

hydrolysis which removes from the solid to the liquid phase part of the protein substance."

If we try to apply these considerations to gels containing glycerin, it would seem that either type or structure, or indeed a combination of both, could account for their behaviour at constant temperature. Glycerin undoubtedly is a dehydrating agent, and if the solid phase is poor in water to begin with, the withdrawal of even a small fraction of the latter may account for the increase in modulus caused by the presence of, say, 30 per cent. of glycerin in the dispersion medium. This, as has already been pointed out, is in agreement with the simplest interpretation of the diffusion experiments. On the other hand these can, without any very forced assumptions, be reconciled with Poole's second, and preferred, type of structure: since gelatin is "insoluble" in absolute glycerin, increasing concentration of the latter in the liquid phase would reduce the amount of gelatin in solution in the liquid phase and increase the volume of solid phase with a consequent increase of the modulus. If this hypothesis is adopted, the greater rate of diffusion with increasing glycerin content, compared with the calculated value, may be explained as follows: with increasing glycerin content the amount of gelatin dissolved in the liquid phase becomes less, and the lowering of viscosity due to this cause may quite conceivably overbalance the increase in viscosity caused by the higher glycerin concentration. Since all these factors may be operative, it is perhaps not surprising that even at constant temperature the connection between glycerin concentration and modulus is not a simple one. Here the demonstration, furnished for the first time by the present work, that the modulus keeps changing for months, introduces a fresh difficulty by raising the question what the final state of the gel would be if it were kept throughout at constant temperature. Every change of temperature produces a change in the gel which, while probably reversible, is likely from all we know to be so with considerable hysteresis; the effect of 50 or 60 such cycles makes interpretation hopeless. The first step towards elucidating and, perhaps, formulating quantitatively the relation between modulus and glycerin content would seem to be the study of ageing at constant temperature, a course which, in view of the probable duration of the experiment, presents considerable technical difficulties.

The rate at which deformation becomes irreversible (Fig. 9) will also have to be studied in these conditions, especially if the part played by the viscosity of the liquid phase is to be defined. The effect of increasing the glycerin concentration on the rate of relaxation is evidently much simpler than that on the modulus, and is in qualitative agreement with the assumption that this rate is controlled by the flow of the liquid phase through the fibrillar network of solid phase. The changes in the latter are much less obvious and any conjecture regarding them has to explain the fact, demonstrated here for the first time, that the gel becomes elastically anisotropic, and that the modulus in the direction of dilatation becomes greater than the original modulus of the isotropic gel. This fact has to be viewed, together with the other effects of both reversible and irreversible deformation known up to the present, viz.:

- (I) In permanently deformed bodies of gel the tensile strength is a minimum in the direction of compression; <sup>1</sup>
- (2) During reversible deformation the tensile strength is a minimum in the direction of dilatation; <sup>1</sup>
- (3) During reversible and after permanent deformation bodies of gel are isotropic as regards diffusion; <sup>1</sup>

(4) A body of gel on deformation becomes optically anisotropic. If it is kept deformed until the stress has practically disappeared, the optical anisotropy remains unaltered.<sup>7</sup>

All these statements refer to gels containing IO to I5 per cent. of gelatin. The permanent isotropy, under all conditions, in respect of diffusion may be disposed of at once. If diffusion takes place in a liquid phase filling the interstices of a network which occupies a comparatively small fraction of the total volume, it is fairly certain that moderate deformation of the system—the volume of which remains constant—cannot materially alter the aggregate cross-section available for diffusion in any direction.

It is much more difficult to reconcile the optical anisotropy (4) with the anisotropies in regard to tensile strength (I) and (2), and with the elastic anisotropy after permanent deformation, for the following reason: the accidental birefringence which appears as soon as deformation is produced does not change while the deformation becomes permanent, while during the same transition the direction of minimum tensile strength turns through a right angle. The permanent deformation has so far received very little attention in the literature, and when mentioned has been ascribed to plastic yield or fatigue of the fibres, which is not helpful. Poole has attempted to explain the persistence of optical anisotropy with disappearance of stress in terms of his theory, which postulates a reversible hydration or hydrolysis the equilibrium constant of which varies with the temperature: "The persistence of optical strain after the disappearance of all mechanical stress seems capable of explanation by the foregoing theory in that if a molecule be removed by solution from a distorted fibril and then replaced by reprecipitation it will have given up its share of the stress. In this way when all the molecules in the fibril have been replaced the whole of the stress in the fibril will have disappeared, but the fibril will still retain its distorted form. In an undistorted jelly the fibrils may be considered as distributed haphazard in all directions. Any optical effects dependent on the direction of the fibrils themselves will then cancel each other. When the jelly is strained, all the fibrils take a trend towards the line of stress. The geometrical balance of the system is then destroyed and a resultant optical effect will then appear. If the fibrils are then fixed in this position the optical effect will remain although, as shown above, no mechanical stress may be present."

This explanation involves two very considerable difficulties, the first of which existed at the time it was offered. If the equilibrium between the solid and liquid phase is completely defined by temperature, there appears to be no reason why mere stress should cause the "distillation" suggested by Poole, at constant temperature. It is hardly necessary to add that the experiment first described by me in 1920 was not carried out in these conditions, nor were any of the numerous repetitions since. In view of the high temperature coefficient of the modulus, it is conceivable that even small diurnal temperature variations would be sufficient to produce the solution and re-deposition of solid phase suggested by Poole, but this does not help to account for the elastic anisotropies.

Poole assumes that the geometry of the solid network remains unaltered from the application of stress to its disappearance. It would seem a necessary corollary that any mechanical or elastic anisotropies should also be the same at the beginning and at the end of the process of deformation, but this is not the case; the direction of minimum tensile strength, e.g., in the reversibly deformed gel is at right angles to that in

the permanently deformed (I) and (2) above. If an unaltered geometry is assumed, it is necessary to account for this rotation by changes in the fibrils themselves which for the present must be purely a matter of conjecture. It seems necessary to point out that, while the behaviour of the gel at the extreme stages of deformation is fully established, the transition has not been studied; this could probably be accomplished by the airbubble method, but to yield really conclusive evidence the investigation ought also to be carried out at constant temperature. It would be of particular interest to ascertain whether an isotropic stage occurs somewhere between the two extreme anisotropic ones.

As regards, finally, the hardening of isotropic and anisotropic specimens by formaldehyde, attempts at interpretation must necessarily be provisional until the chemistry of the process has been investigated. Of the observed facts the most striking is the enormous absolute increase in the value of E, as shown in Fig. 12; the initial values for the 13 and 15 per cent. gel are (at 9.2°) 428 and 683 gm./cm.² respectively, and the final values in round figures 7.5 and 11.4 kg./cm.² The ratio of the initial values is 1.59 and that of the final ones 1.52, or approximately the same, which is what would be expected on the assumption that the elasticity of the gel is that of the network of fibrils, and that the reaction with formaldehyde raises the modulus of these fibres. This constant ratio is, however, fortuitous; other sets hardened in formaldehyde solution do not show it, and with specimens hardened in vapour the ratio final/initial modulus increases considerably.¹

Some portion of the increase in E must be put down to increased gelatin concentration, since all gels lose water during the process of hardening. The fraction of the original water content thus lost does not depend merely on the composition of the gel, but varies with the concentration of the formaldehyde solution used and becomes largest when hardening is carried out in vapour. The following examples will suffice:

						(Hardened in 2 per cent. solution.)		
					I	per cent.	15 per cent. gel.	
Water lost, pe	r cent	of	origina	al w	ater			
content		•	•		•	8-34	3.95	
					(Ha	rdened in vapour.) 8 per cent.	10 per cent. gel.	
Water lost, pe	r cent	. of	origina	al w	ater			
content			•			21.05	19.15	
Initial modulus						283	366	
Final ,,		•			•	2390	4720	

The loss of water raises the gelatin concentration of the 8 per cent. gel to 9.74, and that of the 10 per cent. gel to 11.93 per cent. Assuming the modulus to vary as the square of the gelatin concentration, 3, 5 and the gelatin to be unaltered, the increase in concentration would raise the modulus of the 8 per cent. gel to 418 and that of the 10 per cent. one to 521. This is an inconsiderable contribution to the total increase, nor is the higher gelatin concentration, judging from a large experience of diffusion experiments, sufficient to account for the reduced diffusion velocity. The most probable hypothesis to account for both effects is the formation of condensation products, for which the disappearance of large amounts of formaldehyde from solution provides at least strong indirect evidence, which will have to be confirmed by chemical investigation of the hardened gel. The observations on the hardening of anisotropic gels, i.e., the regular increase in both moduli, suggests strongly

that any such material is laid down in such a way as to reinforce an existing structure while preserving its anisotropy more or less unaltered. If this view is correct the study of the formaldehyde-hardened gel should help materially to elucidate some outstanding problems, more particularly the changes during and after deformation.

## Summary.

Methods of determining Young's modulus on specimens of gelatin in compression and of preparing accurate test pieces for this purpose have been described.

Examples are given to show (a) that gels containing between 8 and 12 per cent. of dry gelatin have a well-defined modulus for stresses up to about 45 gm./cm.², and (b) that the values of the modulus from two determinations at different stresses on the same test piece, and at the same stresses on duplicates having the same history agree within about 3 per cent.

The moduli of gels containing various percentages of cane sugar or glycerin have been determined, and the results disagree with those of earlier investigators. Both cane sugar and glycerin raise the modulus above that of aqueous gels, but there is no simple relation between the increase and the sugar or glycerin concentration; the temperature-modulus curves of gels with 50 per cent. of glycerin intersect the curves for 40 per cent. in one or two points. The discrepancies are believed to be due to ageing which proceeds at different rates with the different concentrations and with the temperature cycles through which they have passed. It is shown that the modulus of glycerin gels kept with all precautions increases for two months and probably longer.

Test pieces containing various concentrations of glycerin have been compressed to the same fraction—0.9—of their original length and the percentage of this deformation which has become irreversible measured from time to time. For equal percentages the time required increases with the glycerin content; the ratio of the times in which equal percentages have become irreversible in two gels with different glycerin content is approximately constant. The time factor is very probably a function of the viscosity of the dispersion medium, but the whole process would have to be carried out at constant temperature to get reliable information on this point.

Prismatic test pieces have been permanently compressed, and the modulus in the direction of compression and in the direction of dilatation at right angles to it determined. The former retains about the same value as in the original gel, while the latter becomes considerably greater. Previous work has shown that the tensile strength also increases in the direction of dilatation.

It is pointed out that a complete interpretation of these results is not possible until they have been investigated at constant temperature.

The increase in modulus caused by hardening in formaldehyde solution has been followed. The *E*-time curve has been analysed by reference to the experimentally determined rate of diffusion into a cylindrical surface; this comparison suggests, and determinations of the formaldehyde concentration in the hardening bath show, that a much larger amount of formaldehyde is removed from the latter than can be accounted for by reaction with NH<sub>2</sub> groups. The most probable provisional explanation is the formation of condensation products.

That such products, if formed, are deposited so as to reinforce an existing structure appears to be proved by the behaviour of test pieces permanently deformed and then hardened: both moduli increase regularly. The *E*-time curves of aqueous anisotropic gels show the same sudden change of curvature as those of isotropic ones, while the *E*-time curves of gels containing glycerin are almost straight lines. Attention is called to the effect of glycerin on other processes, such as drying, controlled by diffusion, which it not only retards but modifies.

# THE ABSORPTION SPECTRA OF SOLUTIONS OF IODINE BROMIDE, CYANOGEN IODIDE, AND CYANOGEN BROMIDE.

By A. E. GILLAM.

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In an earlier investigation, the absorption spectra of carbon tetrachloride solutions of the halogens and certain of the interhalogen compounds were studied, the main objects being to obtain absorption spectra data on iodine monochloride and iodine monobromide, and to use these for comparison when seeking evidence of the existence of bromine chloride. Later, a more detailed examination was made of the absorption spectra of iodine monochloride in other solvents. It was shown that this substance is capable of giving solutions the colours of which fall into one of two main classes, yellow, or brown, each colour being associated with a characteristic absorption band. If was further found that this dichroism is closely analogous to that which has long been known in the case of iodine solutions.

The present paper describes the results of an investigation of the related compounds, iodine monobromide, cyanogen iodide, and cyanogen bromide along similar lines.

#### Iodine Monobromide.

The material used was prepared by the direct combination of carefully purified bromine and iodine. Atomic proportions were slowly mixed together with warming and shaking, when the mixture set to a hard crystalline mass melting about 42° C. The purity of the preparation was determined by dropping a weighed portion into potassium iodide solution and titrating the liberated iodine with standard sodium thiosulphate. The amounts of iodine and bromine present were adjusted until the liberated iodine, calculated as IBr, showed that the sample was pure. All the solutions subsequently examined were made by direct weighing of this product into the required solvent.

## Absorption Spectra Measurements.

The determinations of absorption spectra have been made photographically, using Hilger E. 3 quartz spectrographs in conjunction with Hilger sector photometers, the light sources consisting of an iron-nickel arc in air, and a tungsten spark under water.<sup>3</sup> In the absorption curves the molar extinction coefficient, e (or its logarithm in certain cases), has been plotted against wave-length in millimicrons,  $m\mu$ , e being defined by the relation:

$$\log I_0/I = E = ecd,$$

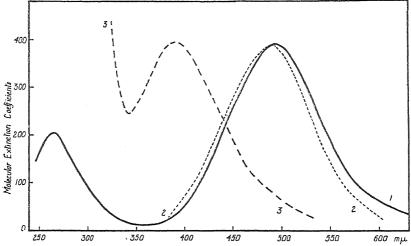
<sup>&</sup>lt;sup>1</sup> Gillam and Morton, Proc. Roy. Soc., 124A, 604, 1929.

<sup>&</sup>lt;sup>2</sup> *Ibid.*,**132A**, 152, 1931.

<sup>&</sup>lt;sup>3</sup> J. McNicholas, Bur. of Stand. J. of Research, 1, 939, 1928.

where  $I_0$  = the intensity of the incident light, I = the intensity of the emergent light, c = the molar concentration, and d = the thickness of the layer of solution in centimetres. The absorption spectra measurements detailed below were obtained on freshly-made solutions, the concentrations used having been (with few exceptions) of the order of 0.02 Molar.

Carbon Tetrachloride Solutions.—In the previous examination of iodine bromide in this solvent <sup>1</sup> the solution was prepared by mixing equimolar parts of iodine and bromine in carbon tetrachloride. Only one absorption maximum was recorded and this varied in different determinations by the visual and photographic techniques between 487 and 494 m $\mu$ . As slight excess of iodine would tend to displace the maximum towards longer wavelengths owing to its own intense absorption in this region, 487 m $\mu$  was then considered to be the correct location of the absorption maximum. In the present investigation the solid iodine bromide was weighed off directly into the purified CS<sub>2</sub>-free carbon tetrachloride, and the absorption spectrum determined photographically. The mean curve obtained from



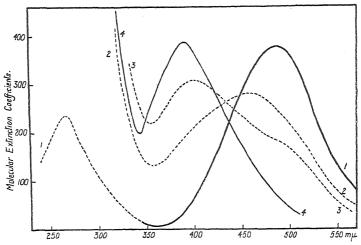
- In carbon tetrachloride.
- In carbon tetrachloride (in the presence of excess bromine to reduce dissociation—compensated for the excess).
- 3. In CCl<sub>4</sub> + 5 per cent. of alcohol (+ a little ozone to remove HI<sub>3</sub>).

Fig. 1.—Absorption spectra of iodine bromide solutions.

a number of observations shows that the maximum is at 494 m $\mu$  (Fig. 1). In order to test whether any dissociation into iodine and bromine occurs in this solvent, the iodine bromide was examined in the presence of excess of bromine. The curve so obtained (Fig. 1) shows a slight displacement of the maximum to 490 m $\mu$ . This is probably a truer value for the absorption maximum of undissociated iodine bromide, but the smallness of the displacement indicates that the dissociation must be quite small. In the earlier examination 2 cm. cells were used, but with this thickness of solution there is appreciable absorption of rays of short wave-length by the solvent itself. By using 1 mm. cells it has been possible to examine the absorption spectrum of the solution further down into the ultra-violet. The new curve (Fig. 1) discloses a second absorption maximum about 266 m $\mu$ .

**Chloroform Solutions.**—In this solvent iodine bromide shows selective absorption with maxima at 487 and 267 m $\mu$  (Fig. 2). The intensity of the latter band varies slightly with different solutions (the dotted portion of

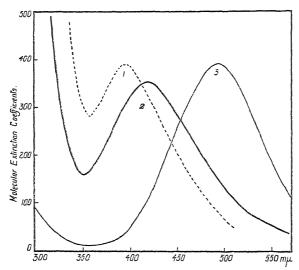
curve 1, Fig. 2, is the mean curve), the variation being apparently due to the formation of traces of HIBr<sub>2</sub> which exhibits highly intense selective absorption in this region (vide infra).



- 1. In alcohol-free chloroform.
- 2. In chloroform + 2 per cent. alcohol)
- 3. In chloroform + 5 per cent. alcohol + ozone to remove HI:
- 4. In pure alcohol.

Fig. 2.—Absorption spectra of iodine bromide solutions.

Alcohol.—Iodine bromide dissolves in pure alcohol to give a solution which, when dilute, is quite yellow, but darkens in colour on standing.



- 1. Ethyl acetate.
- 2. Glacial acetic acid.
- 3. Carbon tetrachloride (for comparison).

Fig. 3.—Absorption spectra of iodine bromide solutions.

Before determining the absorption spectrum of the solution, it was treated with little ozonised oxygen to prevent the formation of hydrogen tri-iodide which exhibits characteristic absorption bands this region.4 curve (Fig. 2) exhibits a maximum at 390 mμ, and is identical both in intensity and location with given that by carbon tetrachloride solutions containing 5 per cent. of alcohol (Fig. 1).

Ethyl Acetate.

—The absorption

<sup>&</sup>lt;sup>4</sup> Batley, Trans. Far. Soc., 24, 438, 1928.

spectrum in this solvent (redistilled, b.p.  $75^{\circ}$  C.) is very similar to that in alcohol, the maximum occurring at 395 m $\mu$  (Fig. 3).

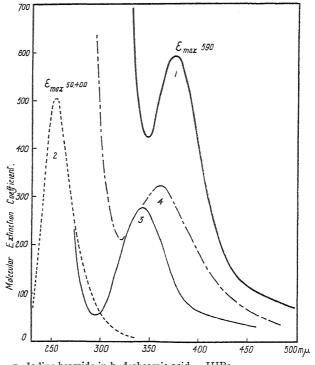
Acetic Acid.—The pure water-free acid gives a solution which is slightly more brown than those in the two preceding solvents. The absorption curve

(Fig. 3) shows a maximum at 419 m $\mu$ .

Hydrobromic Acid.—Aqueous hydrobromic acid dissolves iodine bromide much more readily than the foregoing organic solvents, giving a bright orange-yellow solution. The absorption curve exhibits two maxima at 375 and 253.5 m $\mu$ , the band at 375 m $\mu$  being approximately one and a half times as intense as that exhibited by the solutions already discussed. The fact that the absorption band is of greater intensity as well as being dis-

placed towards shorter wavelengths, indithat cates it owes its origin to some entity other than that responsible absorption in the case of the non-aqueous solutions. 253.5 band at  $m\mu$  is highly intense, the absorption being about eighty times that at the head of the  $375 \quad m\mu \quad b$  This high  $m\mu$  band. intensity of absorption is also in strong contrast with the relatively low absorption otherwise similar 266 mu band in the carbon tetrachloride solutions.

Hydrochloric Acid. — Iodine bromide dissolves just as readily in this



- I. Iodine bromide in hydrobromic acid = HIBr<sub>2</sub>.
   Iodine bromide in hydrobromic acid (continued on Ton scale).
- 3. Iodine monochloride in hydrochloric acid = HICl2.
- 4. Iodine bromide in hydrochloric acid = HIClBr.

solves just as  $_{\rm Fig.~4}.-\!\!$  Absorption spectra of aqueous  $\rm HiBr_2,\,HiCl_2$  and  $\rm HiClBr.$  readily in this

solvent as in the last, giving a yellow solution. The absorption curve shows a maximum at 36r m $\mu$  (Fig. 4), the location and intensity being thus quite different from those of the corresponding band given by the hydrobromic acid solution.

#### The Colours of Iodine Bromide Solutions.

Lachmann <sup>5</sup> has divided solvents into two classes, which he calls "saturated" and "unsaturated," the former giving violet solutions with iodine, whilst the latter give brown solutions. Mixed solvents give

<sup>&</sup>lt;sup>5</sup> Lachmann, J. Amer. Chem. Soc., 25, 50, 1930.

intermediate shades. Iodine monochloride has also been shown to exhibit a similar kind of dichroism with these two classes of solvents.<sup>2</sup>

An examination of iodine bromide solutions reveals the fact that these may also be one of two colours, yellow or red, depending on the type of solvent used. The following table summarises these facts and discloses the parallelism with iodine:—

Solvents yielding with:—  Iodine, violet solutions Iodine chloride, red-brown solutions Iodine bromide, red solutions	Solvents yielding with :—  Iodine, brown solutions Iodine chloride, yellow solutions Iodine bromide, yellow or orange solutions
Carbon tetrachloride Chloroform (alcohol-free) Trichlorethylene Hexane Cyclohexane Benzene Toluene Xylene Carbon disulphide	Methyl alcohol Ethyl alcohol Ether Ethyl acetate Amyl acetate Formic acid Acetic acid Acetone

In the original experiments with iodine, Lachmann 5 used many other solvents, but the above list is sufficiently representative.

The foregoing data show that iodine bromide exhibits dichroism in solution analogous to that shown by iodine and iodine chloride. Taking alcohol and carbon tetrachloride as representatives of the two types of solvent, the absorption maxima for the three compounds I<sub>2</sub>, IBr, and ICl are as follows:—

	Alcohol.	Carbon Tetrachloride.	Difference.
Iodine Iodine bromide Iodine chloride .	447 Μμ	520 mμ	73 mμ
	390 Μμ	494 mμ	104 mμ
	355 <sup>Μ</sup> μ	460 mμ	105 mμ

Since the publication of the previous paper on iodine chloride,<sup>2</sup> and while this work was in progress, Cremer and Duncan <sup>6</sup> observed that iodine bromide solutions show a variation in colour of the same type as that shown by iodine solutions. These authors examined the absorption spectra of a number of solutions, but their observations were mainly confined to the visible spectrum.

In the red iodine bromide solutions it is highly probable, by analogy with iodine and iodine chloride, that the solute is present largely in the state of undissociated molecules. It seems equally probable that the substances iodine, iodine chloride and iodine bromide possess the power of attracting solvent molecules of certain types to form loose addition compounds between solute and solvent, the process being usually referred to as "solvation." Where this occurs the absorption spectrum is quite different from that of a solution containing "unsolvated" molecules. As an example of this the action of alcohol on the carbon tetrachloride solution of iodine is interesting. Thus, I per cent. of

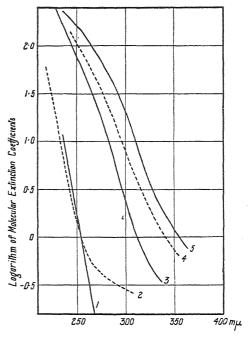
<sup>6</sup> Cremer and Duncan, J.C.S., 2031, 1932.

alcohol alters the colour visibly, but 5 per cent. is required for the colour and absorption spectrum to be changed completely to those characteristic of alcohol solutions (Fig. 1).

A similar phenomenon occurs when alcohol is added to the chloroform solution. The absorption curves of iodine bromide in mixtures of these two solvents show that 2 per cent. of alcohol in the chloroform gives rise to a mixture of the solvated and unsolvated forms, whilst with 5 per cent. of alcohol the change to the solvated form is further advanced, though still not quite complete (Fig. 2). The amount of alcohol required to effect this change is in this case at least fifty times the molar concen-

tration of the iodine bromide present. The relatively large excess of alcohol molecules required to form the solvation complex indicates that this is readily dissociated, and only exists when the mass action effect of the excess of suitable solvent molecules is large enough.

The solutions of iodine bromide in hydrochloric and hydrobromic acids are distinctly different from in the foregoing organic solvents, notably in the location and intensity of the absorption bands. That these bands are due to the substances HIBrCl and HIBr<sub>2</sub> respectively, or their anions, is strongly supported by the work of Cremer and Duncan 7 who have clearly shown that these compounds exist in Absorption spectrum of: such solutions. There is a steady displacement of the maximum towards longer wave-lengths, as well as an increase in intensity of absorption, as we pass from



- I. CNBr in pure chloroform.
- 2. CNBr inpure alcohol.
- 3. CNI in pure alcohol.
- 4. CNI in chloroform + 10 per cent. alcohol.
- 5. CNI in pure chloroform.

HICl<sub>2</sub> through HIClBr to HIBr<sub>2</sub> (Fig. 4). The absorption spectra of these acid solutions are similar to those recorded by Gilbert, Goldstein and Lowry 8 for the cæsium, potassium and certain organic polyhalides and their ions. That solutions of this third class contain more definite compounds, and are different in nature from the solvated and unsolvated iodine bromide solutions, is shown by adding one drop of pyridine to a solution of iodine bromide in carbon tetrachloride. The colour changes at once to bright yellow, and in a few minutes the compound C<sub>5</sub>H<sub>5</sub>N. IBr separates out.9

9 Williams, J.C.S., 2783, 1931.

<sup>&</sup>lt;sup>7</sup> Cremer and Duncan, J.C.S., 1857, 1931.

<sup>&</sup>lt;sup>8</sup> Gilbert, Goldstein and Lowry, J.C.S., 1092, 1932.

Having examined the compounds I<sub>2</sub>, IBr and ICl, it became of interest to enquire whether the corresponding compounds CNI and CNBr exhibit similar properties. Accordingly, samples of cyanogen bromide (Kahlbaum) and cyanogen iodide (prepared by the action of iodine on potassium cyanide <sup>10</sup>) were obtained, and purified by sublimation.

The absorption curves of cyanogen bromide in alcohol and chloroform respectively (Fig. 5), show that this substance is very transparent to both visible and ultra-violet rays. No evidence of an absorption maximum is shown down to 220 m $\mu$  at least, and as the curves for both solutions are almost identical there is thus no evidence of the dichroism shown by the interhalogen compounds. The term "dichroism" is here extended to cover light-absorption in the ultra-violet as well as the visible region.

Cyanogen iodide, like the preceding compound, is quite colourless in solution. The spectrum (Fig. 5) discloses no absorption maximum (down to 240 m $\mu$ ), but shows more absorption than that of cyanogen bromide. Cyanogen iodide differs also, in that the absorption curve of its alcohol solution is displaced towards shorter wave-lengths compared with that of the chloroform solution. To test whether the light absorption of the chloroform solution is affected by small amounts of alcohol in the same way as that of the true inter-halogen compounds, the cyanogen iodide was dissolved in chloroform containing 10 per cent. of alcohol. The resulting curve was found to be displaced to a position about half-way between those for the two pure solvents (Fig. 5). It is inferred from this that the displacement of the absorption curve of chloroformic cyanogen iodide by alcohol is similar to that which occurs with the true interhalogen compounds, but that the phenomenon is much less marked in this case.

# Summary and Conclusions.

The results of this and previous work, 1, 2, on the absorption spectra of the halogen and inter-halogen compounds in solution, show that:—

I. Iodine bromide exhibits dichroism similar to that shown by iodine and iodine chloride. The yellow solutions (e.g., in alcohol) exhibit an absorption band with a maximum near 400 m $\mu$ , whilst the red solutions (e.g., in chloroform) absorb similarly about 490 m $\mu$  (molecular extinction coefficient in each case 350-400).

2. The hydrobromic and hydrochloric acid solutions are different from those in the ordinary organic solvents, the absorption bands being due to HIBr<sub>2</sub> and HIBrCl respectively, or their anions.

3. The substances Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>, BrCl, ICl and IBr, exhibit broad unresolved bands of selective absorption in the visible or near ultra-violet. On the other hand, the compounds CNI and CNBr are practically transparent in these regions, but both exhibit end-absorption which may be part of a band with a maximum below 220-240 mμ.

4. The substances I<sub>2</sub>, ICl, IBr (and, in a limited sense, CNI) exhibit one or other of two absorption bands according to whether they are dissolved in "saturated" or "unsaturated" solvents (e.g., chloroform and alcohol respectively). This property has not so far been observed in any other of the above substances, and hence would appear to be exclusive to such of these compounds as contain an iodine atom (or atoms).

<sup>10</sup> Abegg and Auerbach, Handbuch anorg. Chem., 4, (ii) 476, 1913.

5. This dichroism, in the case of iodine, has been attributed to the occurrence of solvation by certain solvents, with a corresponding change in absorption spectrum. It would therefore appear that the iodine molecule possesses "residual valency" which makes it capable of forming loose addition compounds with certain types of solvent molecules. The present results show that this residual valency persists even when one of the two atoms in the iodine molecule is replaced by any one of the radicles Cl, Br or (CN).

My thanks are due to Professor E. C. C. Baly, F.R.S., for facilities for carrying out this work, and to Dr. R. A. Morton for his criticism and advice.

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# AN ANALYSIS OF HYDROGEN ADSORPTION PHENOMENA.

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A determining feature in much surface behaviour of hydrogen is the fact that H<sub>2</sub> evaporates far more readily than H<sub>1</sub> from most solids under comparable conditions of temperature, etc. The great variety of experiments involving this feature are distinguishable according to whether (i) the H<sub>1</sub> is produced from H<sub>2</sub> in the gas phase by electric discharge or other disturbance and subsequently adsorbed on to the solid, or (ii) the H<sub>1</sub> only becomes dissociated at the surface by adsorption forces themselves. In either case adsorbed H<sub>1</sub> may evaporate as H<sub>1</sub> or as recombined H<sub>2</sub> according to the detail of its career on the surface. Such career is often very complex, and has recently begun to be elucidated in the case of (ii) by Lennard-Jones. 1 Much of the earlier knowledge of surface behaviour had been approached through (i), and it will be an important preliminary to the extension of Lennard-Jones' methods to other hydrogen phenomena to determine which of the laws discovered from (i) are valid for (ii), and vice versa. As a contribution towards this, the present paper classifies a large number of experimental data not hitherto shown in relation to one another, and a general equation is constructed in terms of which the equilibria they represent are exhibited as particular cases. Results of this classification are applied to investigating some of the conditions which control the liberation of energy at a surface where adsorption, evaporation, dissociation, and recombination are taking place. Some requirements and limitations characterising thermal study of surface phenomena are then determined and related to the commoner methods of studying adsorption by pressure measurement.

<sup>&</sup>lt;sup>1</sup> Lennard-Jones, Trans. Faraday Soc., 28, 333, 1932.

# PART I. ANALYSIS INTO EQUILIBRIA.

# Summary of Experimental Data.

- A. When  $H_1$  impinges on a solid from the gaseous phase its subsequent behaviour leads to one of the following:—
- I. Specular reflection as  $H_1$  after interval no longer than vibration period of lattice; e.g., experiments of Stern, T. H. Johnson, and others, on crystal surfaces.
- 2. Re-evaporation as  $H_1$  after interval long compared with vibration period; e.g., experiments of R. W. Wood, Langmuir, and others, on transmission of  $H_1$  along narrow channels involving many wall collisions.
- 3. Evaporation as  $H_2$  after recombination with gas atom or with another adsorbed atom; e.g., experiments of R. W. Wood on heating of tungsten, platinum, glass, in streams of  $H_1$  mixtures, also of Bonhoeffer on series of metal surfaces.
- 4. Existence as stable layer in static equilibrium or in variously maintained kinetic equilibria; e.g., experiments of Langmuir on  $H_1$  derived from hot wires, of M. C. Johnson on  $H_1$  from electrodeless discharge and from photo-sensitised dissociation.
- $\mathbf{B.}$  When  $\mathbf{H_1}$  diffuses from the interior of a solid to its surface there is evidence that there occurs :—
  - 5. Evaporation from the surface as H<sub>2</sub>, not as H<sub>1</sub>.
- C. When H<sub>2</sub> impinges from the gaseous phase, its subsequent behaviour leads to one of the following:—
- 6. Re-evaporation as unchanged H<sub>2</sub> with loss or gain of kinetic energy only; e.g., experiments of Knudsen and others on the type of encounter which allows random direction of evaporation, and which is describable in terms of a fractional "accommodation coefficient" or efficiency of energy transfer.
- 7. Evaporation as H<sub>1</sub>; e.g., experiments of Langmuir with hot tungsten filaments.
- 8. Evaporation as H<sub>2</sub> with transformation into spin-isomer, probably involving successive dissociation and recombination; e.g., experiments of Bonhoeffer, Hartek, Farkas, Egerton, and others, on orthohydrogen and para-hydrogen at metal and charcoal surfaces.
- 9. Existence as stable structure, commonly as constituent of complex double or multiple layer, as in the sensitised surfaces of alkali photoelectric cells.
- 10. Diffusion into the solid as  $H_1$  after dissociation at surface; e.g., experiments of Ward and others leading to Lennard-Jones' explanation of the mechanics of  $H_2$  in collision with a strongly attracting surface.

# Generalised Kinetics of Condensation and Evaporation in Mixtures.

Simultaneous adsorption from several components presents an almost untouched subject of prohibitive complexity, but in hydrogen the very divergent nature of the alternatives for  $H_1$  and  $H_2$  enables progress to be made by constructing a general equation and then determining which portions are negligible for which type of experiment.

Let  $n_1 = \text{number per cm.}^2$  on surface at any moment, of particles of type I.

 $n_2 =$  number per cm.<sup>2</sup> on surface at any moment, of particles of type 2, etc.

 $v_1 =$  number striking surface from gas phase, per sec. per cm.<sup>2</sup>, of particles of type 1.

 $v_2$  = number striking surface from gas phase, per sec. per cm.<sup>2</sup>, of particles of type 2, etc.

In particular cases the term "on the surface" needs defining as "with centre of particle within given distance of centre of nearest member of solid lattice," and hence may not have the same meaning at different crystal faces.

Collecting the several sources of gain and loss of particles to and from the surface

$$\begin{array}{l} \mathrm{d} n_1/\mathrm{d} t = \alpha_1 \nu_1 - (\beta_1 + \gamma_1) n_1 + \phi_1(\nu_1 \ldots \nu_n, n_1 \ldots n_n) \\ \qquad \qquad - \psi_1(\nu_1 \ldots \nu_n, n_1 \ldots n_n), \\ \mathrm{d} n_2/\mathrm{d} t = \alpha_2 \nu_2 - (\beta_2 + \gamma_2) n_2 + \phi_2(\nu_1 \ldots \nu_n, n_1 \ldots n_n) \\ \qquad \qquad - \psi_2(\nu_1 \ldots \nu_n, n_1 \ldots n_n), \text{ etc.} \end{array}$$

 $\alpha$ ,  $\beta$ ,  $\gamma$  are coefficients proportional to the chances, respectively, of adsorption, evaporation, and absorption into the solid, and are of dimensions suited to the homogeneity of the equation.  $\phi$  and  $\psi$  are functions of the surface density and gas concentration of the several types of particle, representing respectively the formation of particles of type I from other types, and the formation of other types at the expense of type I, etc. In the most important case with which we deal,  $\phi_1$  and  $\psi_2$  express the functional dependencies of dissociation, and  $\psi_1$  and  $\phi_2$  those of recombination of atoms to molecules. For most purposes  $\alpha$  may be taken as unity.  $\beta$  and  $\gamma$ , representing spontaneous evaporation and diffusion, exhibit only the comparatively simple dependence on temperature of Boltzmann's factors; in particular we may write,

$$\beta_1 = \theta_0 \beta_{10} e^{-E_{10}/KT} + \theta_1 \beta_{11} e^{-E_{11}/KT} + \dots + \theta_n \beta_{1n} e^{-E_{1n}/KT}$$
, etc.,

where  $E_{10} = \text{work done in evaporating a particle of type I from the bare surface,}$ 

 $E_{11} =$  work done in evaporating a particle of type I from the surface covered with particle of type I,

 $E_{12}$  = work done in evaporating a particle of type I from the surface covered with particle of type 2, etc.,

and the  $\theta$ 's are the fractions of surface thus variously covered. The E's involve lateral intermolecular forces between adsorbed particles themselves as well as normal forces between them and the solid surface (p. 1152 below).

# Conditions for Monomolecular Structure in Static and Kinetic Equilibrium.

The physical interpretation of the above equations is seen when they are reduced to their simplest form, equivalent to Langmuir's isotherm. This occurs if  $H_1$  and  $H_2$  are present as gaseous constituents, as in any electric discharge, but if no surface dissociation or recombination occurs, and no diffusion into the solid. The  $\beta$ 's for  $H_1$  and  $H_2$  are then inversely proportional to  $\tau$ , the "Verweilzeit," or time elapsing between arrival

and departure at the surface, a quantity first investigated by Frenkel.<sup>2</sup> If we define a state of equilibrium by

$$dn/dt = 0$$
,

it is clear that suitably chosen values of  $\nu$  allow both large and small values of  $\tau$  to characterise very different adsorbed structures possessing equal values of n. It is hence convenient to classify such layers as in "static" or "kinetic" equilibrium, according as individual particles remain long on the surface between each adsorption and desorption, or have only small  $\tau$  but are so rapidly replaced that statistically a large value of n is maintained.

Following this distinction, the common terms "saturation," denoting completion of growth of a layer, must have different meanings according as n is limited only by the intrinsic repulsions between closely packed particles, or by the rate at which a looser structure is being lost and

replaced in kinetic equilibrium.

In the limit of smallest "Verweilzeit,"  $\tau$  may be no greater than half the vibration period of the solid lattice; this occurs in cases better classed as "reflection," where no exchange of energy takes place between gas and solid, "evaporation" being spoken of only when there is finite energy exchange. "Evaporation," with which we are exclusively concerned in this paper, takes place in random directions according to a cosine law of distribution distinct from the specular reflection discussed in the wave mechanics of boundary encounters. [Experimental data I.]

Many modern experimental methods depend upon the attainment of a steady gas pressure, hence upon adsorption being separated from absorption, and upon saturation being completed with monomolecular thickness of layer. The author and other workers have proved particular circumstances to guarantee saturations in static and kinetic equilibria when even fewer atoms have been deposited than would pack a single layer. In view of the importance of knowing when adsorption is to be strictly monomolecular—e.g., thermo-chemical or thermionic phenomena at a filament's surface must not be masked by the filament's response to the continued pressure changes which would accompany the growth of any thicker layer—we develop in detail some of the conditions governing such surface structure. In terms of the general equation above, if for any gas

$$(a) E_{11} \ll E_{10},$$

then any layer subsequent to the first deposited will be very weakly held in static equilibrium, causing cessation of growth at monomolecular thickness. But if

$$(b) E_{nn} \gg E_{n0},$$

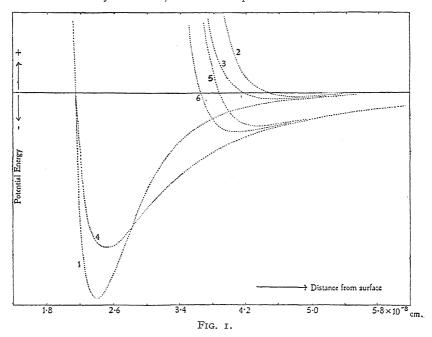
then subsequent layers can be strongly held by the cohesion between the gas particles themselves being greater than their common adhesion to the surface. Frenkel pointed out the multimolecular adsorption of metallic vapours according to this law, and we draw attention below (p. 1145) to the rare instance of its occurrence in hydrogen.

(c) If  $E_{10}$  is large and  $E_{11}$  small but  $E_{21}$  . . . is large, a "sandwich" of two or more substances, each of monomolecular thickness, may occur. This is of importance for thermionic and photo-electric emitters in

oxygen and alkali vapours, and for photo-electric emitters in hydrogen

also. [Experimental data 9.]

For the particular case of hydrogen, (a) is not the only source of restriction of an adsorbed layer to monomolecular thickness, since the function  $\psi_1$  in the general equation allows  $H_1$  the possibility of recombining and desorbing as  $H_2$ , thus contributing to the prevention of a thicker layer developing in kinetic equilibrium. In view of the very complex variations we find later (p. 1148) in  $\psi_1$ , it is important to obtain quantitatively the limits to the more general condition (a) for monomolecular structure. In Fig. 1 we plot as potential energy of a gas particle arriving at an exposed surface the algebraic sum of attractive and repulsive energies; the repulsion curve alone is then displaced outward from the solid by a distance equivalent to the collision diameter of an atom already adsorbed, and this displaced curve is then combined



with the previous attractions to the surface to denote the energy of a particle in any second layer which might be adsorbed on the top of the first. This approximation gives quantitative expression to condition (a) for a molecular model in which the first layer is itself inert towards the gas, and in which the compressibility of the gas particle and of the solidr atoms are the same; it probably represents fairly closely the behaviou' of  $H_1$  in those cases where the gas and the layer do not recombine. The values of such energies of attraction and repulsion are only exactly known in certain limited cases, but for the purpose of finding the limits to the validity of (a) it is quite sufficient to distinguish between models possessing the "short range" attractions familiar between matter capable of a homopolar bond and the "long range" for dipole structures of similar compressibilities. Assuming a repulsive energy of the inert gas type varying inversely with the 12th power of distance, curve I shows its

combination with attractive energy varying with an inverse 6th power, for a ratio of attractive and repulsive coefficients chosen to give a minimum in the curve at 2.4 Å.U. from the solid. Curves 2 and 3 represent similar energy/distance laws for the same attraction if a monomolecular layer of the gas is already present on the surface. In 2 the thickness of the layer is 1.4 Å.U., and has reduced the depth of the minimum in the curve, i.e., the atomic heat of adsorption of the second layer, by a factor of nearly 60, while in 3 the thickness is 1.2 Å.U., and similarly reduces adsorption energy of any second layer by a factor of nearly 40. Hence, while temperature is still low enough for the monomolecular layer to be perfectly stable, all subsequent deposits will be easily vaporised.

In contrast, curve 4 shows a dipole attraction varying with an inverse 3rd power combined with the same repulsion as before. Curves 5 and 6 represent the masking of this attraction by monomolecular layers 1.4 and 1.2 Å.U. thick, which here reduce the subsequent adsorption minima by factors of 5 and 4 only. Hence, for gases and vapours adsorbing by virtue of dipolar properties, saturated monomolecular equilibrium, according to the general condition laid down, will only be possible over a more limited range of temperature, a second layer vaporising comparatively shortly before the first layer itself begins to become unstable.

## Classification of the Experimental Data as Types of Equilibrium.

Most knowledge of the adsorbed phase has been obtained through measurements, e.g. of pressure fall, in the gas phase; also, in the most important exception to this, namely thermionic studies of surface conditions, changes in gas pressure have to be carefully allowed for through the necessity already mentioned (p. 1142). Hence, experimental data are most conveniently distinguished according to whether, and for what reason, H<sub>1</sub> can exist in the gaseous state near any surface.

Type I. 
$$\begin{array}{c} \nu_1 = \text{ o,} \\ E_{10} \ll D, \\ \vdots \quad n_1 = \text{ o.} \end{array}$$

Here D is the work done in separating two normal atoms to infinity from the normal state of  $H_{2}$ , *i.e.* under most conditions the heat of dissociation. For most solids we have

$$E_{10} \gg E_{20}$$
.

Hence in this case, with no atomic gas present, there is also not sufficient surface attraction to produce an atomic layer by breaking up impinging  $H_2$ , itself weakly held. Hence  $n_1$ ,  $\phi_1$ ,  $\psi_1$ ,  $\phi_2$ , and  $\psi_2$  have zero value in the general equations.  $\gamma_2$  is shown to be negligible by all experiments on the sharing of hydrogen between evacuated vessels whose walls are non-metallic and smooth, though when a surface is of loosely aggregated or spongy material, diffusion of  $H_2$  itself may be considerable.

The only equilibrium possible is a kinetic one maintained by high gas pressure at low temperature. Inserting in the general equation the equilibrium condition (p. 1142) the non-zero terms left may be written:—

$$\alpha_2 \nu_2 = n_2 (\theta_0 \beta_{20} e^{-E_{20}/KT} + \theta_2 \beta_{22} e^{-E_{22}/KT}).$$

 $E_{22}$  is of the order of 500 cal./mol. only, and since for many solids  $E_{20}$  is even less, layers of more than one molecule thick condense before a

single sheet is fully packed. For instance, at the initial stages of bulk liquefaction in vitreous vessels H<sub>2</sub> may here obey the law more commonly found in metallic vapours (p. 1142).

The above conditions, securing zero value of certain terms in the general equation, are necessary in obtaining unambiguous data on accommodation coefficients [Experimental data 6], where the only energy exchange between the phases must be that of translational, vibrational, or rotational kinetic energy of the unchanged H<sub>2</sub>.

Lennard-Jones <sup>1</sup> has given an explanation of this existence of  $H_1$  in an adsorbed layer when there was none in the gas, by developing pairs of graphs in which ordinates represent the potential energy of  $H_2$  and of  $2H_1$  with respect to the solid at various distances from the surface. In the case of most interest  $H_2$  is held by the surface forces weakly at a greater distance than  $H_1$  is held strongly, as illustrated by the depths and positions of the two "troughs" or minima in the curves. If  $H_2$  has sufficient kinetic energy to reach the intersection of the two curves it may make a transition into the  $2H_1$  curve, dissociating and becoming adsorbed  $H_1$  without work being done. Conversely, if adsorbed  $H_1$  reaches the intersection (generalised to a "critical surface" in three dimensions) by gain of kinetic energy from the solid, it can recombine if it there encounters other  $H_1$ .

The need of energy for  $H_2$  to reach the intersection enforces a maximum probability of dissociation at a particular temperature, giving rise to the term "activated" for this adsorption by dissociation. The form of variation of  $\phi_1$ , the corresponding function in our general equation, as the temperature is taken above and below such an optimum, is not yet known; but we can discuss some important features by assuming gas and solid to be not far from that temperature, *i.e.*, we approximate to the case in which every molecule striking the bare solid dissociates, and write:—

$$\phi_1(\nu_1 \ldots \nu_n, n_1 \ldots n_n) \doteq \alpha_2 \nu_2(1 - \theta_1).$$

In most cases  $E_{10}$  is too great for evaporation at ordinary temperatures, and hence

$$\beta_1 n_1 \doteq 0.$$

Therefore, for equilibrium of the layer of H<sub>1</sub> on the surface,

$$\alpha_2 \nu_2 (\mathbf{I} - \theta_1) = \psi_1(n_1) + \gamma_1(n_1),$$

and for any adsorption of undissociated H<sub>2</sub> which may occur where the bare solid is shielded by a covering of H<sub>1</sub>,

$$\alpha_2 \nu_2(\theta_1) = n_2(\theta_1 \beta_{21} e^{-E_{21}/KT} + \theta_2 \beta_{22} e^{-E_{22}/KT}),$$

which last could be investigated by graphs of the type we used above in Fig. 1.

Three particular cases of the equilibrium of surface-dissociated  $H_1$  are of importance in interpreting the experiments.

(a) At the lowest temperature compatible with efficiency of this dissociation, the atoms are unable to escape either by diffusion into the

solid or by lateral migration leading to recombination with their fellows, so that

$$\psi_1 = \gamma_1 = 0.$$

The layer fills up until at  $\theta_1 \to \mathrm{I}$  it constitutes a rigid extension of lattice structure into the gas, one atom thick, the spacing not necessarily being the same as that of the solid; this exemplifies "saturation" in the first sense of p. II42. Such a solid-like adsorbed layer in static equilibrium presents the greatest contrast to the fluid-like layer of type I., and is probably that found by Davisson and Germer 3 in their study of the surface properties which cause diffraction patterns with cathode rays. Since very low temperature has to be reached before a detectable loss of pressure occurs over a solid already covered with  $\mathrm{H_1}$ , the quantity  $E_{21}$  must be extremely small, and its actual magnitude can be evaluated by the method of Fig. I; but it is possible that superposed  $\mathrm{H_2}$  affects considerably the rate of recombination of the underlying  $\mathrm{H_1}$ , and vice versa that an  $\mathrm{H_1}$  layer may affect the subsequent condensation of  $\mathrm{H_2}$  on the walls of liquefaction apparatus.

(b) If  $\psi_1 \neq 0$ , we have the case of Experimental data 8, where  $H_2$  evaporated from a solid is found to possess different nuclear spin properties from those of the impinging  $H_2$ , fresh molecules having been formed after dissociation of the original gas. The equilibrium is now no longer static, and the rigid layer has acquired more or less of lateral mobility, saturation density being now limited by the rate of re-evaporation after recombination.

(c) If  $\gamma_1 \neq 0$  there is an additional source of loss from the lever through diffusion of atoms into the solid, further modifying the saturation value allowable to  $n_1$ . The non-zero limiting fall of pressure observed in Experimental data 10 most probably represents this form of kinetic equilibrium.

Type III.—If the temperature is now raised until an evaporation term is no longer negligible in spite of the magnitude of  $E_{10}$ ,  $H_1$  may appear in the gaseous form independently of any agency in the gas phase causing dissociation. Langmuir's  $^4$  pioneer study of the properties of  $H_1$  is an example of this [Experimental data 7], the atoms being dissociated at a hot filament and evaporated therefrom. The terms of importance to equilibrium are then

$$\alpha_2 \nu_2 (1 - \theta_1) = n_1 \theta_0 \beta_{10} e^{-E_{10}/KT} + \psi_1(n_1) + \gamma_1(n_1).$$

At such temperatures ( $> 1300^{\circ}$  C.)  $\tau$  for  $H_2$  is so small that  $n_2$  is negligible. Langmuir's hydrogen is sometimes spoken of as thermally dissociated, and in Part II. below we draw the necessary distinction between this and dissociation of the type II. which can occur at lower temperatures, by analysing the sources of the energy increments involved.

The third, or diffusion, term of the right hand side is of much greater importance here than in type II., and probably underlies the experiments of Dillon on the disappearance of hydrogen into a tungsten filament of even small area.

It is clear that by adjustment of  $\psi_1$ , towards which we develop some considerations below, and by choice of T, it may be possible to find a substance and set of conditions at which both dissociation and recombina-

<sup>&</sup>lt;sup>3</sup> Davisson and Germer, Physic. Rev., 30, 705, 1927.

<sup>&</sup>lt;sup>4</sup> Langmuir, J. Am. Chem. Soc., sequence of papers 1912-19.

tion proceed at optimum rates; such investigation must underlie advances in the control over the para-ortho-hydrogen changes. [Experimental data 8.]

**Type IV.**—The only existence of gaseous  $H_1$  so far considered, in Type III, required evaporation of atoms already present in the dissociated form on the surface. But certain aspects of surface behaviour can only be investigated by creating free atoms through agencies themselves confined to the gas phase and independent of surface properties. [Experimental data I, 2, 3, 4.] For instance, most vitreous materials, e.g., the walls of apparatus, are such that

$$E_{10} \ll D$$
.

This precludes the development of any atomic layer except by condensation of  $H_1$  which has already had a gaseous existence before encountering any surface. Since the dissociating agent can now be controlled and intermittent, instead of being an ever-present surface, the relations between  $\nu_1$  and  $n_1$  can be investigated manometrically with assurance that the surface is initially "empty" and "finally saturated"; whereas with the more strongly adsorbing metal surfaces of Types II. and III. a zero value of  $n_1$  was never possible once the surface had been exposed to the slightest trace of  $H_2$ , so that the number of atoms needed for packing a saturated layer was essentially inaccessible to investigation.

The "hardening" of spectroscopic and discharge apparatus thus offers material not available with metal adsorbents, and by eliminating the latter in electrodeless and photo-sensitised dissociation I have isolated <sup>5</sup> Type IV. from II. and III. for the study of  $n_1$ ,  $\beta_1$ , and  $\psi_1$ . [Experimental data 4.] The vitreous surface, however, essential through its freedom from surface dissociation, is also essentially subject to large errors in estimation of "accessible area."

Type V.—Except when radiative or electrodeless means are adopted for producing  $H_1$  in the gas phase, there must always be exposed some metallic surface, and if any of these are such that

$$E_{10} > D/2$$
,

dissociation by surface action will be added to that taking place in the gas. If such surfaces include very hot filaments, as in some thermionically maintained discharges, all the preceding types of equilibrium may be found superposed,  $H_1$  being not only present in the surface layer because previously in the gas, but also evaporated into the gas after previous dissociation at and existence on the surface.

#### Processes of Recombination.

In the many chemical and physical experiments which will be subject to the complexity mentioned as characterising Type V., the controlling factor is commonly the allocation of recombination between the two possible processes,

$$H_1$$
 (ads.) +  $H_1$  (ads.)  $\rightarrow$   $H_2$  (desorbing),  
 $H_1$  (ads.) +  $H_1$  (gaseous)  $\rightarrow$   $H_2$  (desorbing).

Both of these are included under the function  $\psi_1$  of p. 1141, and Types IV. and V. might exhibit both in various proportions. In the author's and

<sup>&</sup>lt;sup>5</sup> M. C. Johnson, *Proc. Roy. Soc.*, **123**, 603, 1929; **132**, 67, 1931; *Proc. Physic. Soc.*, **42**, 490, 1930.

other workers' experiments with vitreous surfaces, recombination of the first kind, which we represent by  $\psi_1$ ,  $n_1^2$ , has been proved to vanish to a high approximation at ordinary temperatures. The second kind,  $\psi_1\nu_1n_1$ , must, on the other hand, vanish in the absence of  $\nu_1$ , which characterises Type II. Although the complete form of  $\psi_1$  is not determinable from isolated instances, it is important to decide its dependence on the commoner variables, for the interpretation of other data as they emerge. I owe to a remark of Professor Lennard-Jones a suggestion as to certain variations of the ratio between the probabilities of the two processes,

$$R = \psi_1 \nu_1 n_1 / \psi_1 n_1^2$$
.

Let  $P_1$  be the probability that an adsorbed atom acquires from the solid sufficient energy E to reach the intersection of the molecular and atomic curves (p. 1145). Let  $P_1'$  be the probability of a neighbouring adsorbed atom reaching the same point at the same time.  $P_1$  and  $P_1'$  are each controlled by the factor  $e^{-E/KT}$ . On the other hand,  $P_2$ , the probability of a free atom from the gas reaching the same point, will vary with  $\nu_1$ , the stream density striking unit area, and also with the fraction of unit area which is the target for capture of the adsorbed atom. For a reason mentioned below (p. 1149), this target area may either be associated with an atom or a space between atoms, but may in either case be reasonably taken as  $2 \times 10^{-16}$  cm.<sup>2</sup>

Hence, if other conditions are constant,

$$\begin{array}{l} R = P_1 P_2 / P_1 P_1' \\ = [(e^{-E/KT})^2 \times 10^{-16} \nu_1] / (e^{-E/KT})^2 \\ = 2 \times 10^{-16} \nu_1 / e^{-E/KT}. \end{array}$$

In Table I. is shown the variation of this ratio as E, T, and  $\nu_1$  are allowed to range sufficiently to cover many common cases arising out of the experiments we have mentioned. For most of these

$$p_1 \ll p$$

where  $p_1$  is the partial pressure of  $H_1$  and p the total gas pressure, itself commonly less than a millimetre. The table indicates the conditions under which surface recombination may occur more frequently between adsorbed  $H_1$  and gaseous  $H_1$  than between adsorbed pairs, and *vice versa*, other things being equal. The point at which, *e.g.*, a change of temperature may reverse any preponderance can be derived for any particular set of conditions by reading off corresponding values of E,  $\nu_1$ , T, on a logarithmic plot.

# TABLE I.

The simplification of the above by constancy of all other conditions may become invalidated by the following consideration. Since in quantum mechanics two  $H_1$  atoms in collision may exhibit either mutual attraction leading to formation of stable  $H_2$ , or mutual repulsion of the

kind more familiar in the rare gases, the ratio R must also involve the determining conditions of these alternatives, generally described physically in terms of the sign of spin of the constituent electrons. For an isolated pair of atoms these are known, but the fact of their being held to the surface may alter the conditions profoundly, to an extent not calculable in the present state of physics.

When the time comes for such determining conditions to be evaluated theoretically it may be of importance to make more precise the definition of " $H_1$  (ads.)" in the above reactions, by introducing the refinement suggested on p. 1141. It is possible that intrinsic probability of recombination between an impinging gas atom and an adsorbed atom may vary from zero to unity or vice versa according as the encounter is a head-on collision or a partial penetration of the gas atom into the interstices of the adsorbed layer. Since I have proved experimentally  $^5$  that a saturated  $H_1$  layer is not closely packed, the penetration may in some cases be complete enough for  $\psi_1\nu_1n_1$  as well as  $\psi_1n_1^2$  to be considered as representing reaction "in" the layer; the distinction between the alternatives whose ratio we calculated as R, would then be a distinction as to immediate previous history of the reactants rather than as to their present situation.

# PART II. THERMAL PHENOMENA.

# Exchanges of Energy in Molecular Transitions.

Owing to the minute thermal capacity which suitably small metallic objects may possess, these provide a means of obtaining direct measurement of the energy exchanges occurring when hydrogen impinges on dissociating, adsorbing, and recombining surfaces, sometimes rising to very high temperatures owing to the liberation of some portion of  $E_{10}$  and of D. [Experimental data 3.] This feature of surface behaviour may even become of technological importance, as in Langmuir's welding apparatus. Hitherto it has not been possible to ascribe unambiguously any variations in such heating to differences in intrinsic adsorbing power, in recombination facility, or merely in density of impinging stream of  $H_1$ , and it has never been made clear to what types of adsorptive equilibrium any particular source of heat liberation may be confined. Some considerations towards this are here put forward.

Consider a case of the kinetic equilibrium Type V. above, in which the more important terms may be written:—

$$\alpha_1 \nu_1 (\mathbf{I} - \theta_1) + \phi_1 \nu_2 (\mathbf{I} - \theta_1) = \psi_1 n_1^2 + \psi_1 \nu_1 n_1 + n_1 \theta_0 \beta_{10} e^{-E_{10}/KT}. \quad (\mathbf{I})$$

The left-hand side represents adsorption from gaseous  $H_1$  and adsorption with dissociation from  $H_2$ , and the right-hand side represents recombination between pairs of adsorbed  $H_1$ , between adsorbed  $H_1$  and impinging gaseous  $H_1$ , and finally the spontaneous evaporation of  $H_1$ .

The maximum energy absorbable from or returnable to the solid in these several processes may be exhibited graphically, as the algebraic sum of the differences of level in the "troughs" in all the potential diagrams expressing the transitions included under equation I. This simple summation is, however, necessarily confined to exhibiting the maximum only, the extent to which any solid actually rises in temperature being a function also of conductivity and other losses, as well as of specific heat, and further, of intrinsic probabilities of the various transitions, a subject scarcely begun to be investigated.

Let  $A_1$  be the negative potential energy at the minimum of the adsorption curve for  $H_1$  (e.g., in Fig. 1), and D the work of dissociating two normal atoms to infinity. Let  $K_1$ ,  $K_1'$ , be initial and final kinetic energies of an  $H_1$  atom before reaching and after leaving a surface, and  $K_2$ ,  $K_2'$ , the corresponding quantities for  $H_2$ . These will include vibrational and rotational energy for particles possessing such degrees of freedom. Then the total energy available for liberation at the surface per unit time per unit area during the state of kinetic equilibrium represented by equation I is  $\Sigma(N, E)$ , where N', N'', N''', etc., are the number of transitions per sec. per cm. 2 contributed by each term of the equation, and E', E'', E''', etc., are the particular combinations of  $A_1$ , D,  $K_1$ ,  $K_1'$ ,  $K_2$ ,  $K_2'$ , associated with the several terms as energy set free per transition per atom. These combinations are given in Table II.

#### TABLE II.

For each loss and gain of an atom an amount of energy K representing its vibration level in the adsorbed state will be added to and subtracted from, respectively, the above values of E. In the net liberation of energy during a cycle of gain and loss the contributions of this K cancel out.

# Application to Particular Types of Equilibrium.

We proceed to combine the above values of N and E into sequences appropriate to certain of the types of adsorptive equilibrium classified in Part I. as underlying the various experimental data.

Type II.—Consider the three particular cases described on p. 1145.

(a) Once the state of equilibrium is established there is no further loss or gain of particles to the rigid layer, and therefore no further exchange of energy between gas and solid, except that of the elastic encounter specified by the accommodation coefficient. But until  $\theta_1 \rightarrow I$  the quantity  $[A_1 - D/2 + K_2/2 - K]$  is liberated at each adsorption of an  $H_1$ : this quantity must be positive in order to obey the condition for the existence of this kind of adsorption, making more precise the simpler criterion which sufficed for its classification in Part I.

(b) When the equilibrium is kinetic instead of static, and controlled by recombination, the latter can only occur between adsorbed pairs, i.e., R is zero because  $\nu_1$  is zero, and equation I reduces to

$$\phi_1 \nu_2 (I - \theta_1) = \psi_1 n_1^2.$$

Each further adsorption is now only made possible by the vacating of a region of surface by recombination and desorption, hence the positive potential energy liberated is balanced by that absorbed, and if final and initial kinetic energies are equal

$$\Sigma(E) = 0.$$

But in the more general case

$$\Sigma(E) = K_2/2 - K_2'/2.$$

The important conclusion is that a solid at whose surface such a reversible cycle is proceeding cannot rise or fall in temperature other than by the usual mechanism of conduction, however dense the adsorbed layer or however rapidly replacement and re-adsorption is taking place.

(c) If, however, some additional source of loss of  $H_1$  from the surface occurs, the number of adsorptions is now no longer equal to the number of recombinations, but to the total number of losses; e.g., diffusion into the solid may prevent desorption from completely neutralising the thermal effects of adsorption.

Type III.—If high temperature allows the vibrational level of adsorbed  $H_1$  to rise till its relation to the solid is no longer expressible by a trough in the energy curve (Fig. 1), there occurs the additional loss of  $H_1$  from the layer by spontaneous evaporation. If this process be isolated from the other sources of loss we have

$$\phi_1 \nu_2 (I - \theta_1) = n_1 \theta_0 \beta_{10} e^{-E_{10}/KT}.$$

Adding the appropriate values of E as before from Table II.,

$$\Sigma(E) = -D/2 + K_2/2 - K_1'.$$

Thus the solid loses 50,000 cal. per gm. atom of adsorbed H<sub>1</sub>, less any deficiency of desorbing compared with initial energy.

We distinguish here between two alternative ways of regarding Langmuir's hot-wire dissociation referred to on p. 1146. (a) Assume the dissociation is "thermal," i.e., due to thermal equilibrium with a surface which itself has not enough attracting power to dissociate the gas except by virtue of its high temperature. (b) Assume it can occur at the much lower temperatures which might allow a maximum efficiency of Lennard-Jones' mechanism.

In case (a),  $H_2$  is adsorbed at a low level in the curve of molecular energy relative to the solid, and the adsorbed molecules then acquire sufficient vibrational energy to carry them to what may be a very high point of intersection with the atomic curve. As  $H_1$  in its new adsorbed position a certain further increment then raises it to a still higher level in the atomic curve until it evaporates with kinetic energy  $K_1$ . Here the work done by the solid may be considered as mainly employed in the process of dissociating the  $H_2$ .

In case (b) more of the required energy is obtained while in the atomic state, which was itself more easily reached. Here the work done is mainly employed in evaporating atoms, which had already been dissociated owing to the low level at which the curves intersect at this particular surface.

The expression for  $\Sigma(E)$  above is readily verified as formally valid for each of these alternatives, the net result of desorption of particles with potential energy D/2 greater than those impinging, being thus independent of the adsorbing power of the solid.

Langmuir's discovery that a monomolecular layer of  $O_1$  inhibits the dissociation of  $H_1$  at a hot wire suggests that (b) is the preferable view, and that the inhibition is due to a screening similar to that which we illustrated in Fig. I.

Types IV.=V.—When H<sub>1</sub> is present in the gaseous state, either alone (Type IV.) or in addition to that produced by surface forces themselves, this may cause, instead of the loss of energy by the solid in the preceding case, a gain of energy or heating, which has been used to investigate

several molecular properties.<sup>6</sup> The terms in equation I contributing to this are the two in  $\psi_1$ , between which some of the laws of variation have already been discussed. Since each of these liberates the same energy per adsorbed atom, although in the first of them two such are always involved simultaneously, the net energy liberated in either sequence may be taken, from Table II.,

$$\Sigma(E) = D/2 + K_1 - K_2'/2.$$

This is the source of heat which has been known to raise small vanes or wires to incandescence in an electric discharge.

It is important to notice that in this particular process the heat of adsorption  $A_1$  disappears from the expression for maximum energy available for heating the surface, as it also did in the cooling effect (p. 1151). Hence loss and gain of heat from this particular source is a function of kinetic energy and heat of dissociation alone, so long as variations in  $A_1$  from one substance to another do not alter the statistical balance between the several processes. This consideration is essential in applying calorimetric methods to surfaces involving hydrogen and other diatomic gases, and illustrates the control over these phenomena of the following principle: heat given to the solid can only be derived from a positive difference between initial and final kinetic or potential energy of a gas particle. Hence, in cyclical operations of the surface forces alone no heating can be set up, and the conclusion of p. 1154 (b) is of very wide generality.

# Consequences of Rise in Temperature.

The sensitiveness of certain of the surface processes to change in temperature, e.g., Table I., makes it important to note what other alterations in adsorptive equilibria are to be expected if the temperature of a surface is raised. This may occur by deliberate alteration of the current supplied to an adsorbing strip or filament, or may be due to such of the energy liberations we have discussed, as conductivity, etc., allows to become apparent. In the present state of the subject, only a qualitative list of temperature effects is possible, and between these the particular combinations may be very complex.

(a) If those of the adsorbed atoms which do not recombine merely approximate to inert gas particles in their weakness of mutual attraction, then (i) the function  $\phi_1$  plotted against T passes through a maximum, (ii) R falls with rise of T, (iii) lateral mobility increases with T, (iv) spontaneous evaporation increases with T. Since the underlying processes are interdependent, and where their variation includes factors of the form  $e^{-E/KT}$  the respective E's are of widely different magnitudes, it is clear that the net rate of energy liberation is capable of passing through more than one maximum as temperature is raised. The position of any maximum with respect to T will again depend on whether  $\nu_1$  and  $\nu_2$  are large enough to maintain  $n_1$  constant while the rate of loss of particles from the layer is being accelerated.

(b) But if, further, the adsorbed particles are capable of cohering among themselves, the work needed to move an atom from its equilibrium position will no longer be A but [A+A'], where A' represents the heat of disintegration of any structure formed by such mutual cohesion, and is accordingly itself a function of  $n_1$ . In some substances mutual cohesion hinders re-evaporation, while in others the evaporation probability per

particle seems to decrease at lower concentrations, depending on whether dipole or other forces predominate between the adsorbed particles. Since quite large attractions are now attributed to hydrogen atoms in certain non-combining states,  $^7$  a layer of  $H_1$  is not exempt from this complication. In some measurements with tungsten wire independently maintained at various temperatures in a stream of  $H_2$  and  $H_1$ , I recorded a maximum in the rate of liberation of energy plotted against initial temperature, and this maximum probably represents some particular combination of the above factors.

# Graphical Example of Thermal Phenomena during a Sequence of Pressure Changes due to Adsorption.

As an example in applying the foregoing analysis a graphical treatment is included of the way in which the several processes may be expected to combine in underlying a complex of observed phenomena, calorimetric and manometric. We adopt idealised molecular models whose energy levels are of an order of magnitude likely to characterise common experiments. In order to exhibit the essential features independently of those belonging to particular circumstances we assume there is no difference between initial and final kinetic energy in the gas phase, and also that the positive energy available,  $\Sigma(N, E)$  (p. 1150) is all transferred to the solid, giving rise to appropriate temperature changes observable in the latter. Corrections to such approximation would be required for particular hot and cold gases, and particular adsorbents of large or small thermal capacity and conductivity. We further assume that any changes in temperature do not themselves alter the balance between the several processes, also that spontaneous evaporation of H<sub>1</sub> is negligible, and that dissociation at a surface capable of such (Type II.) is proceeding at the maximum rate assumed on p. 1145.

In Fig. 2 are shown ideal graphs relating pressure to time and rate of heat liberation to time, for two surfaces referred to as "metal" and "non-metal" according as they are or are not favourable for the surface dissociation of  $H_2$ . This distinction, though fitting a majority of cases, is not universal, as some metals may adsorb more weakly than some non-metals. The heat of adsorption of  $H_1$  on the metal is of the order of 60,000 cals., and on the non-metal, 10,000 cals.  $t_1$  marks the attainment of any steady state due to surface dissociation, and  $t_3$  any steady state due to a dissociation (e.g., by discharge) which commenced in the gas phase at  $t_2$ . The relative heights of ordinates are roughly to scale, but the units are arbitrary, depending on such things as ratio of volume to surface in apparatus used, and type of dissociating agent chosen.

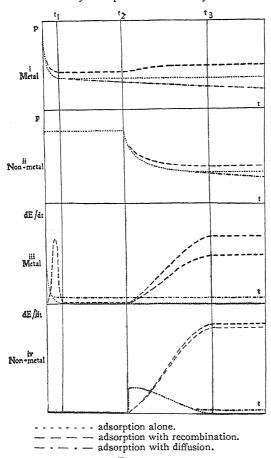
The following features are illustrated, some explicitly derived in the preceding sections, others implicit.

- I. If, as is usual, the partial pressure of  $H_1$  in the gas is small compared with that of  $H_2$ , a steady state may far more quickly be reached in adsorption by surface dissociation than in adsorption of the gaseous atoms. Hence the approach to  $t_1$  is in general less accessible as an observable datum than the approach to  $t_3$ .
- 2. If diffusion into the solid occurs, it not only prevents attainment of a steady state of pressure, (i) and (ii), but may allow constant liberation of some fraction of the available heat of adsorption after kinetic

<sup>&</sup>lt;sup>7</sup> Eisenschitz and London, Z. Physik, 60, 523, 1930.

equilibrium has been established, due to the vacating of surface area for re-adsorptions on previously occupied spaces (iii) and (iv).

3. When a layer is maintained in kinetic equilibrium by recombination, the observed pressure fall in the gas may be slightly less than in static equilibrium, (i) and (ii), and may become still less the greater the concentration of  $H_1$  in the gas; this effect will, in general, be larger than any pressure variation due to change in molecular weight by the reaction in the gas phase. If the rate of recombination is itself a function of surface density the pressure fall may deviate from a simple exponential



law. In a previous paper I have explored the use of such deviations as a means of investigating recombination, but in general the observed pressure fall may involve several variables.

4. When H<sub>1</sub> in the gas phase is added to that dissociated at the surface, its effect on the pressure graph may be confined to a slight rise due to recombination, (i). But if there is no H<sub>1</sub> already present through surface dissociations a large pressure fall must occur at exposure to gaseous H<sub>1</sub>. On the other hand, the effects on any accompanying thermal observations will be large, whether H, were already present through surface action or not. Hence a thermal sequence of observations may reveal the presence of gaseous H<sub>1</sub> while the pressure sequence conceals it, invalidating comparison between in-

ferences from the two types of measurement.

5. During establishment of equilibrium at the metal surface in the absence of gaseous  $H_1$ , the emission of energy of recombination rises temporarily to a maximum, (iii), but during establishment of equilibrium with  $H_1$  gas in the absence of surface dissociation it is the heat of adsorption which appears transiently, with an initial maximum, (iv).

6. Since recombination between pairs of adsorbed atoms contributes nothing to net heat liberation if they both originated in surface dissociation (p. 1151) no heating appears in equilibrium, (iii), until H<sub>1</sub> appears in

the gas, in spite of the fact that concentration of adsorbed  $H_{\rm I}$  may be nearly the same before and after dissociation in the gas begins.

- 7. A further result of (6) is that when a non-metallic surface is exposed to the same partial pressure of gaseous  $H_1$  the heat liberated at recombination may actually be greater, (iv), than at the far more strongly absorbing metal (iii), and comparison between two such surfaces cannot be used in deducing relative concentrations of  $H_1$  or adsorbing powers. This is because at the non-metal any recombinations between adsorbed pairs do not have their thermal effects cancelled by compensation as at the metal.
- 8. Owing to the greater heat of adsorption at the metal (60,000 cals. compared with 10,000), the additional liberation of energy in the steady state, due to re-adsorptions on spaces vacated by recombination, plays a greater part in (iii) than in (iv), so long as the absorptions are from gaseous H<sub>1</sub>. The added effect of these re-adsorptions is shown in the higher curves of (iii) and (iv). On the other hand, the initial liberation of heat of adsorption is not greatly different in the two cases, since 50,000 out of the 60,000 cals. is taken up in dissociation.
- 9. The maximum height to which the curve representing heat of recombination could rise is ND/2, and since D is of the order of  $10^5$  cals. this would be several times as high as the curve for heat of adsorption, the latter being, for the reason (8), about the same  $10^4$  cals. for metal and non-metal. Actually the recombination curve is always reduced by a multiplier (1-f), where f is the fraction of  $H_1$  atoms which is repelled on striking a layer of  $H_1$ . For the case illustrated f is of the order of 0.6.

# THE KINETICS OF THE THERMAL AND PHOTO-CHEMICAL REACTION BETWEEN IODINE AND DIAZOACETIC ESTER IN CARBON TETRACHLORIDE SOLUTION.

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A general survey of reactions in solution shows that the theory of collisional activation offers the best prospect of co-ordinating the diversified phenomena encountered in this field. The method of applying the theory has been worked out only in those rare cases where experimental conditions appear to be so favourable as to justify certain simple postulates. Even then, there is no general agreement among investigators, nor, in fact, is such to be expected so long as there remains any obscurity about the true nature of solutions. In the meantime, the experimental approach to the problem is open, and indeed inviting. There have hitherto been found only a small number of simple bimolecular reactions between unionised molecules in non-polar solvents. Such reactions offer the ideal conditions concerning which the kinetic theory is able to give safe predictions. That few have been discovered is hardly surprising, for the factors which make them interesting theoretically are precisely those which make them difficult practically.

The present work deals with experimental investigations of the reaction between iodine and diazoacetic ester in carbon tetrachloride solution—a reaction which prima facie is very suitable for the purpose

$$I_2 + N_2CH \cdot COOC_2H_5 \rightarrow N_2 + I_2CH \cdot COOC_2H_5$$

at hand. The evidence afforded, however, is not conclusive, for two reasons. (I) The velocity of reaction is extremely sensitive to impurity. Although all possible precautions have been taken to exclude traces of moisture—which seems to be the most insidious agent—and to work with pure reactants and solvent, it can never be certain that our most favourable conditions correspond to complete desiccation. In the later stages of the work, however, slow and reproducible velocities were found which can probably lay claim to some accuracy. (2) The primary reaction, which is undoubtedly bimolecular, is followed by a second reaction, and possibly by yet a third. We have therefore been driven to concentrate on the determination of the initial velocity, although in each experiment the whole course of the reaction has been followed. Since, however, one of the subsequent reactions is attended by the regeneration of iodine to an extent which varies with the temperature, it is possible that the observed rate of reaction, even in its initial stages, is composite. It will be shown later that there are two possible means of interpreting the experimental results. According to one of these, there is complete agreement between our observations and the predictions of the kinetic theory. According to the second, there is a discrepancy of 60.

The present reaction, whichever interpretation may prove to be correct, clearly approximates in its initial stages to the conditions which have been described as "ideal." Other bimolecular chemical changes in carbon tetrachloride solution have previously been studied with interesting results. One proceeds by consecutive stages, both of which have commensurate rates, so that the velocity for either reaction cannot be evaluated. A second reaction is kinetically simple, but although bimolecular in character, is in reality a catalysed unimolecular reaction.<sup>2</sup> For both these changes, the absolute rates lie near the values calculated by the theory of collisional activation. A third and a fourth reaction, however, in the same solvent—carbon tetrachloride—have velocities about one million times lower than the theoretical values.3 There can be little doubt as to which of these two categories the present reaction belongs.

### Preparation of Materials.

Diazoacetic ester was prepared in the following way. Dry hydrogen chloride was streamed through a boiling suspension of 50 grams of glycine in 120 c.c. of ethyl alcohol which had been freshly refluxed over quicklime. The syrupy liquid, formed when the glycine hydrochloride had dissolved, was frozen, and the excess alcohol drained off. The yield of ethylglycine hydrochloride was 80 per cent.; 60 grams of this compound were shaken with sodium nitrite and a little water; 36 c.c. of ether were added, and the mixture was cooled to 5° C. After treatment with a few drops of dilute sulphuric acid, the ethereal layer was separated from the well shaken mixture. The aqueous layer was further extracted with ether until it

<sup>&</sup>lt;sup>1</sup> Moelwyn-Hughes and Hinshelwood, Proc. Roy. Soc., 131A, 186, 1931.

Lowry and Traill, ibid., 131A, 177, 1931.
 Moelwyn-Hughes and Hinshelwood, Trans. Chem. Soc., 230, 1932.

became colourless. Very small quantities of sodium carbonate were added until the solution was just faintly alkaline. After standing over calcium chloride during the night, the ether was removed, first on a waterbath and subsequently by evacuation. The crude ester was distilled in small fractions, boiling at 53° C./17 mm. The distillate was kept in sealed vessels in the dark. With aqueous acid, the sample of diazoacetic ester thus prepared gave the theoretical yield of nitrogen. Most of our experiments were performed using this preparation of ester, but one or two runs were carried out with a Kahlbaum specimen, from which the solvent (alcohol) was removed in a desiccator over sulphuric acid.

Specially pure carbon tetrachloride, supplied by Messrs. Albright and Wilson, was fractionated in about twenty batches from phosphorus pentoxide. A second sample of the solvent had been kept saturated with chlorine in a glass-stoppered bottle exposed to daylight for two years. After washing with alkali, dilute acid, and finally with water, it was dried

over calcium chloride and distilled from phosphorus pentoxide.

Solutions were prepared by weight, and were stored in glass-stoppered bottles in a desiccator over phosphorus pentoxide.

#### Experimental Procedure.

The reaction was followed in an all-glass apparatus, the air-inlet and the pipette of which were fitted with ground glass joints to phosphorus

pentoxide tubes. These, in turn, were connected with pressure tubing to calcium chloride tubes (not shown in Fig. 1), and thence to the pump. The reaction chamber was covered with two or three layers of tin foil, glued on. Three reaction vessels of this type have been used, their capacities ranging from 20 to 70 c.c., and the pipettes delivering from 0.5 to 5 c.c. Before each experiment, the clean vessel was heated in a large luminous flame or in a steam oven, after which a current of dry air was drawn through it until it reached the temperature of the thermostat. Two burettes, from which the solutions of the reactants were run in, were similarly treated. Vigorous shaking is required after adding the second reactant. Samples of the reaction solution from time to time were run into a measured excess of standard sodium thiosulphate, and titrated against dilute aqueous iodine until the non-aqueous layer showed no trace of colour.

With very dilute solutions, a different technique was adopted. Known volumes of the two reactant solutions were sealed off in dark tubes, which were subsequently broken, the contents of each tube being analysed separately.

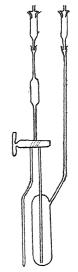


Fig. 1

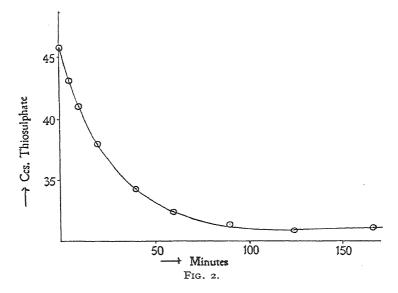
### Experimental Results.

The results of a typical experiment are given in Table I., and are

#### TABLE I

IADLE	5 l.
Time in Minutes.	C.c. of o o1222 N Thiosulphate
0	45.70
5	43.00
10	40•92
20	37 <b>·</b> 86
40 60	34*25
60	32.44
90	31•40
124	30-95
167	31.26
1352	34 <sup>-</sup> 05

represented graphically in Fig. 2. They refer to 3.87 c.c. samples of a reaction solution which contained, initially, ester and iodine at molar concentrations of 0.03483 and 0.07216 respectively at  $45^{\circ}$  C. The two features which call for comment here are (1) the apparent end-point, *i.e.* 



the minimum titration value, does not correspond to equimolar amounts of iodine and ester, and (2) after the apparent end-point is reached, a subsequent reaction sets in or continues, with slow regeneration of iodine. With regard to the first effect, it happens that at 25° C. two molecules of

TABLE II.

t° C.	$[Iodine]_0 \times 100.$	[Ester] <sub>0</sub> × 100.	$k \times 10^4$ .
25	2·415	2·064	7·15
	2·470	2·060	5·74
	1·235	1·005	3·85
	5·250	7·210	5·43
	5·250	7·210	6·27
	4·641	7·210	4·43
	2·600	7·210	4·79
30	3.965	7.210	7.02
35	3·526	7·372	13·3
	3·965	7·930	12·5
	3·965	7·930	10·4
45	3·965	7·930	52·5
	3·230	6·460	44·5
	7·216	3·483	48·8
	2·100	3·870	53·8

ester are used up for each molecule of \_\_ iodine. This suggested that primary reaction is followed by a second reaction, wherein the products attack molecule fresh of ester. The second reaction appeared to be rapid because, with the concentration of ester and iodine in the ratio of 2:1, satisfactory bimolecular constants were obtained. In event, the regeneration of iodine could be regarded as a third reaction, proceeding so slowly as to be of negligible influence.

Photochemical experiments, to be described later, cast doubt upon this supposition, for there it appears that the regeneration of iodine is rapid. The fact that the apparent end-point shifts with temperature disqualifies

the use of the bimolecular equation. For this reason, and on account of the difficulty experienced in reproducing results, we have abandoned the prospect of giving an interpretation of the kinetic phenomena over the complete course of the reaction, and have adopted the method of initial rates.

The order of reaction was determined by two methods. Four concordant experiments conducted at 25° C., with ester and iodine at a concentration of 0.01 molar, gave a half-life of 22.6 hours. With double the concentration, four other experiments showed the time of half-completion to be 10 hours. Within the limits of reproducibility, the reaction has thus been proved to be bimolecular. The same result has been obtained in a more convincing manner by altering the concentration of iodine by a factor of 10. The bimolecular constants, calculated from the initial velocities, were  $2\cdot37\times10^{-3}$  and  $2\cdot04\times10^{-3}$  for two runs at  $45^{\circ}$  C.

As already indicated, the results obtained during the early stages of the investigation were very erratic. They are reproduced in Table II. in the order in which they were found. The bimolecular "constants" refer to the initial velocity, and are given in the units of gram-molecules per litre per second. Subsequently, however, lower values of the velocity were consistently found, which were, moreover, in better agreement with This state of affairs coincided roughly with the use of a new consignment of carbon tetrachloride, and may be due to its greater purity, or to the improved technique which by that time had been realised. The latter explanation is the more probable, because the marked influence of water was not brought home to us until about half-way through the work, when it was discovered that a sample accidentally wetted gave an initial velocity three times as great as the dry sample. The purposeful addition of water to the extent of about 0.04 molar increased the rate by a factor of 7.5. We are therefore justified in accepting the slowest constants as the reliable ones, and in rejecting the high values as due to stray catalytic effects. Without the positive evidence that water hastens the reaction, other possibilities would be equally valid. The slow, and much less erratic, constants found in the later stages of our investigation are summarised in Table III.:-

TABLE III.

			$k \times 10^4$ (litres/gram-molsecond).			
<i>t</i> ° C.	[Iodine] <sub>0</sub> × roo.	[Ester] <sub>0</sub> × 100.	Observed.	Average.	By the Arrhenius Equation.	
45	3·965 3·432 1·375 5·047 0·343	7·93° 5·175 5·175 6·844 5·175	27.0 23.7 26.2 21.3 20.4	23.7	24.8	
35	3.045	3.045	9.24	9.24	8.79	
30	3.927	7.210	5.33	5.33	5.01	
25	2·470 3·430	2·010 5·175	2·65 2·68	2.67	2.84	

# The Molecular Statistics of the Thermal Reaction.

It will be recalled that the results lend themselves to two interpretations. (I) If the reaction which regenerates iodine plays no important

part during the initial stages, the results as given here summarise the position in the correct way. The figures given in the last column of Table III. have been obtained from the Arrhenius equation, which takes the form

$$k = 2.21 \times 10^{11} \times e^{-20,230/RT}$$
.

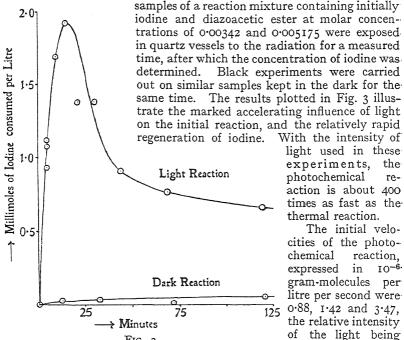
The observed value of the non-exponential term is thus in complete agreement with that given by the expression

$$\frac{N_0}{1000}\sigma_{1,2}{}^2 \Big\{ 8\pi^{RT} \Big( \frac{1}{M_1} + \frac{1}{M_2} \Big) \Big\}^{\frac{1}{2}},$$

indicating that each activating collision leads to chemical change. If the regeneration of iodine is rapid, and immediately follows the primary reaction even in the early stages, the constants given above must. all be increased by a small factor, which is dependent on the temperature. On this basis, the critical increment becomes 17,420 calories, and the chemical efficiency of activating collision is reduced to I in 60.

## Photochemical Observations.

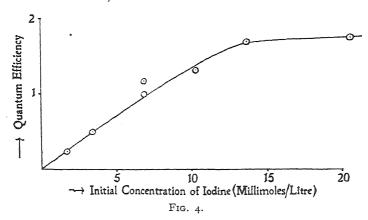
The influence of light was studied at room temperatures (18-19° C.), using a water-cooled quartz-mercury lamp with suitable filters; 18 c.c.



light used in these experiments, photochemical action is about 400 times as fast as the thermal reaction.

The initial velocities of the photoreaction. chemical expressed in gram-molecules litre per second were 125 0.88, 1.42 and 3.47, the relative intensity of the light being I: I:47:3:03.

observed rate is therefore approximately proportional to the intensity. The quantum efficiency of the reaction was measured, using the green line ( $\lambda = 5460 \text{ Å}$ ) of the mercury spectrum. The data are summarised in Fig. 4, and Table IV. The number of molecules of iodine transformed per quantum of energy absorbed seems to be independent of the concentration of ester, but to increase with the initial concentration of



iodine to a limiting value. The highest quantum efficiency found is 1.74, which is 13 per cent. less than 2. The calibration of the thermopile had an error of about this magnitude, each scale division on the gal-

vanometer corresponding to  $6.8 \times 10^{-5}$  calories per second  $\pm 12$  per cent. A limiting quantum efficiency of 2 thus seems to be reached in solutions of moderate concentration.

# Summary.

The kinetics of the thermal and photochemical reaction between iodine and diazoacetic ester have been investigated experimentally in carbon tetrachloride solution.

Reproduction of results referring to the thermal

TABLE IV.

$[Iodine]_0 \times roo.$	[Ester] <sub>0</sub> × 1000.	Quantum Efficiency.
1.71	5·175	0·25
3.42	5·175	0·55
3.42	5·175	0·58
3.42	5·175	0·39*
3.42	5·175	0·49
6.84	5·175	1·00
6.84	10·35	1·09
10.3	5·175	1·31
13.7	5·175	1·70
20.5	5·175	1·74

<sup>\*</sup> This figure refers to the yellow line  $(\lambda = 5780 \text{ Å}).$ 

reaction has been rendered difficult by the powerful catalytic influences of adventitious impurities, particularly water, and by the occurrence of consecutive reactions. Two hypotheses account equally well for the observations made. Upon one of these, the observed velocity is exactly equal to that predicted by the simple collision theory. Upon the second hypothesis, the experimental rate is low by a factor of 60.

Four other reactions are known which occur between unionised molecules in non-polar solvents. Two of these have velocities equal to those calculated by making certain simple assumptions; the others fall short by a factor of one million. The present reaction, in spite of some uncertainty, definitely approaches the conditions which, in the light of the simple theory of collisional activation may be regarded as normal.

The reaction is hastened by light, the effect being proportional to the intensity. The quantum efficiency increases with the initial concentration, reaching a limiting value of 2.

We wish gratefully to acknowledge the valuable assistance given us by Mr. C. N. Hinshelwood, F.R.S., and Mr. E. J. Bowen. We are indebteded also to the Royal Commissioners for the Exhibition of 1851.

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# THE KINETICS OF THE OXIDATION OF PICRIC ACID BY POTASSIUM PERMANGANATE IN AQUEOUS SOLUTION.

By F. F. Musgrave and E. A. Moelwyn-Hughes.

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Many chemical reactions of the second order in aqueous solution have velocities lower than those predicted by the theory of simple collisional activation on the assumption that the observed critical increment is identical with the energy of activation. The assumption may, of course, be in error, but the rate of reaction calculated on this basis offers a useful, if only temporary, standard of comparison. The most notable instances of slow reactions are the hydrolysis and saponification of esters. There are certain other examples, but their number is not large nor the type of chemical change very extensive. It therefore becomes important to discover whether the apparent slowness of these reactions is confined to a limited class or whether it is encountered when dealing with chemical changes of a more unusual kind. With this end in view, we have investigated the kinetics of the following reaction:—

$$3C_6H_2(NO_2)_3OH + 28MnO_4^- + 19H^+$$
  
 $\rightarrow 18CO_2 + 9NO_3^- + 28MnO_2 + 42H_2O$  . (1)

In spite of its stoichiometric complexity and the indisputable existence of consecutive reactions, the observed velocity is governed by a simple process of the second kinetic order.¹ The experiments which revealed this conclusion were directed chiefly at a study of the stability of the benzene ring, as reflected by the relative rates of oxidation of different substituted derivatives of phenol, and were restricted to one temperature. In the present work, the kinetics of the reaction have been examined in greater detail and under wider experimental conditions.

As in the earlier work, the experimental method has been to estimate the concentration of permanganate by adding excess of acidic potassium iodide, and then titrating the liberated iodine against standard solutions of sodium thiosulphate, using starch. All the reagents were chemically pure. Before proceeding to the kinetic studies, special experiments were carried out to discover the fate of the two reactants.

During the oxidation of picric acid, oxides of manganese are precipi-

<sup>&</sup>lt;sup>1</sup> Hinshelwood, Trans. Chem. Soc., 1180, 1919.

tated. The oxidising agent may therefore react wholly as in equation (2), or partly as in equation (2) and partly as in the commoner equation (3). To settle the question, excess of

$$2MnO_4^- + 2H^+ \rightarrow 2MnO_2 + H_2O + 3O$$
 . (2)

$$2MnO_4^- + 6H^+ \rightarrow 2Mn^{++} + 3H_2O + 5O$$
 . (3)

permanganate (initial titre,  $T_0$ ) was allowed to react with picric acid for a period equal to ten times the half-life at 25° C. The oxides were filtered off, and the filtrate titrated  $(T_\infty)$ . The precipitated oxides were then dissolved, added to the first filtrate, and titrated again (T'). The ratio

$$\frac{\text{Iodine value of precipitated oxides}}{\text{Iodine value of complete sample}} = \frac{T' - T_{\infty}}{T_0 - T_{\infty}};$$

the numerical value of the ratio would be 0.4 or zero in the event of process (2) or process (3) occurring exclusively. The experimental value of the ratio is given in Table I.

[Picric Acid] × 10 <sup>3</sup> (Gram-moles/litre).	Duration (hours).	$(T_0-T_\infty).$	$(T'-T_{\infty}).$	$\left(\frac{T'-T_{\infty}}{T_{0}-T_{\infty}}\right).$
2·4	74	18·45	7·45	0.404
4·5	74	34·58	13·82	0.400
2·4	90	19·20	7·90	0.411
4·5	90	35·39	14·22	0.402

TABLE I.

The second series of preliminary experiments were made to determine the number of atoms of oxygen required in the oxidation of I molecule of picric acid. As before, a known amount of the acid was allowed to react with an excess of acidic permanganate at 25° C. for a few days. The difference between the initial and final titres (the latter referring to the complete sample, with redissolved oxides) enables one to calculate the amount of oxygen consumed. The figures in the last column of Table II.

TABLE II.

C.c. of 0°0382 Molar Picric Acid.	Duration	C.c. of one	Number of Atoms of	
	(Hours).	Initially.	Finally.	Oxygen per Molecule of Picric Acid.
0·74 2 2 2 1 2 1	96 72 90 72 72 72 243 243	12·85 26·69 26·28 49·27 49·27 49·27	5·13 20·76 21·17 27·96 37·85 25·02 35·37	14·15 14·10 14·40 14·68 15·73 16·68

show that, provided we confine attention to solutions not too rich in permanganate and to periods of reaction not greatly in excess of ten times the half-life, I molecule of picric acid requires 14 atoms of oxygen, thus corresponding to the requirements of complete oxidation.

$$C_6H_2(NO_2)_3OH + 14O \rightarrow 6CO_3 + 3HNO_3$$
 . (4)

The total reaction given by equation (1) results when equations (2) and (4) are compounded. As will be noticed, more than 14 atoms of oxygen appear to be used up under certain conditions. The reason for this is that acidic solutions of permanganate, even in the complete absence of

#### TABLE III.

25° C. [Picric acid]<sub>0</sub> = 0.001 M. [Permanganate]<sub>0</sub> = 0.0467 N = 0.00933 M. [Sulphuric acid]<sub>0</sub> = 0.020 N. 10 c.c. samples.

t (minutes).	C.c. 0'1038 N Thio.	k × 10 (litre/gram-mol sec.).
0	46.00	
10	44.12	1.23
20	42.68	1.17
35	40.69	1.17
60	38.10	1.15
8 <b>o</b>	36.48	1.13
120	34.03	1.11
165	31.98	1.09
210	30.47	1.07
275	28.80	1.06
œ Č	19.00	

oxidisable bodies, deteriorate slowly at 25° C. Blank experiments, with no picric acid present, showed that an initial titre <sup>l.</sup> of 50·19 fell to 47·91 216 hours. after After allowing for this loss, the high values in the last column of Table II. are reduced considerably, though exactly to 14. The slow and independent decomposition of permanganate must also proceed when

there is picric acid present. This factor probably accounts for the slightly falling values of the bimolecular constants found when the correction has not been applied.

The two familiar expressions have been used in calculating the velocity constants. The time is expressed in seconds, and the

$$k = \frac{2 \cdot 303}{t(a-b)} \log_{10} \frac{T_t(T_0 - T_{\infty})}{T_0(T_t - T_{\infty})},$$
$$k = \frac{1}{ta} \cdot \frac{T_0 - T_t}{T_t - T_{\infty}}$$

concentration in gram-molecules per litre. Thus, in order to have kinetically equivalent amounts of the two reactants, the molar con-

centration of permanganate must be 9.33 times that of picric acid. Alternatively, the normalities of the two must be in the ratio of 46.7: I. Constants calculated on this basis diminish slightly as the reaction pro--ceeds (Table III.). A repetition of this experiment gave the results on Table IV., where, however, a correction of 4 per cent. has been intro-

TABLE IV.

TABLE IV.									
t.	T <sub>t</sub> .	10 k.							
0	47·40 45·66	1.11							
20	44.38	1.01							
31	42.84	1.02							
35	42.24	1.08							
54 80	40.03	1.11							
	37.78	1.10							
121	35.37	1.05							
160	33.47	1.03							
200	32.08	I·O2							
240	30∙80	1.03							
360	28.46	0.98							

Average value of  $k = 1.06 \times 10^{-1}$ .

.duced to allow for the simultaneous decomposition of permanganate.

8.82

The constants given here compare favourably with the value of  $1\cdot 11 \times 10^{-1}$  found by Hinshelwood under similar but not identical

conditions.\* With the concentration of the reactants reduced eight-fold, the following results have been obtained (Table V.). Each sample taken for titration was now 300 c.c. A repetition gave 19 constants in close agreement, the mean value being Satisfactory constants were similarly obtained intermediate concen-

t.	T <sub>t</sub> .	100 k.
0 150 660 870 1080 1380	17·22 16·79 14·53 13·94 13·36 12·70	8·72 8·91 8·73 8·89 8·98

TABLE V.

Average value of  $k = 8.84 \times 10^{-2}$ .

11.70

trations, in the presence of salts and at various temperatures.

2070

 $\infty$ 

# The Influence of Acids and Other Electrolytes.

Some of the earliest observations indicated that the rate of reaction was not markedly affected by the amount of sulphuric ac 1 present. Runs carried out in the absence of acid proceeded with the same initial velocity, but usually fell from about 1.03 × 10<sup>-1</sup> to a fairly constant value of 7.60 × 10<sup>-2</sup> at 25° C. The term "absence of acid" is hardly precise, since picric acid itself is strongly ionised, so that even without sulphuric acid the solution would be rich in hydrogen ions. It has been found, however, that barium picrate reacts with permanganate at much the same rate as free picric acid. The initial velocity was about 0-006, rising this time to a fairly constant value of 7.54 × 10<sup>-2</sup>. The velocity of reaction is thus clearly independent of the concentration of hydrogen ions, but for minor effects which, considering the complexity of the changes, are inconsiderable. One of the reactants is therefore the picric ion.

An attempt to discover whether the other reactant in the rate-

'TABLE VI.

$\sqrt{\mu}$ .	$k \times 10^2$ at 25° C.
0 0·100 0·141 0·200 0·245 0·282	8·13 (extrapolated) 8·84 9·04 9·47 10·4

determining step was neutral or electrically charged was made by studying the influence of the ionic strength on the bimolecular constant. The effect of added electrolytes is a very small one. The presence of OOI N potassium chloride to the solution described in Table III. gave a constant of IO4 × IO-1, i.e., had virtually no effect.

Uni-univalent salts being without effect, the influence of magnesium sulphate, at higher concentrations, was examined. A slight, positive

<sup>\*</sup> The published value of 1·19  $\times$  10<sup>-4</sup> has here been corrected by a numerical factor of  $\frac{2\cdot303}{60}\times\frac{5}{0\cdot000206}$ .

effect was found, similar to that caused by increasing the initial concentration of the reactants. The results obtained are summarised in Table VI., where  $\mu$  denotes ionic strength. On plotting the logarithm of the velocity constant (to the base 10) against the square-root of  $\mu$ , a decided curve is obtained, with a limiting slope of about 0.12. According to the theory of Brönsted, this indicates that the second reactant is possibly unionised. The evidence, however, is inconclusive, as we have been unable to work with solutions so dilute that the Debye-Hückel relation may confidently be applied.

# The Influence of Temperature.

The velocity of reaction at six temperatures may be summarised in the form of the Arrhenius equation,  $k = 1.16 \times 10^6 \times e^{-12,350/RT}$ (Table VII.). The data refer to an ionic strength of 0.01 at all temperatures. With magnesium sulphate present, and the ionic strength at 0.06, the critical increment is 12,760 calories. The difference between the two values of E lies within the limit of our experimental error, so that we may conclude that the critical increment is independent of the ionic strength. This again suggests, but does not prove, that one

TABLE VII.

	k  imes 10 (litres/gram-mole-second).				
t° C.	Observed.	By the Arrhenius Equation			
25·0 34·3 41·0 48·9 54·9 59·8	0·904 1·65 2·47 4·33 6·17 8·78	0.902 1.71 2.66 4.34 6.18 8.17			

reactant may be unionised.<sup>2</sup> Abnormal variations of E with ionic strength have been found for two reactions 3

The observed velocity of reaction may now be compared with the values calculated on two of the simplest assumptions. (I) If we accept the value of

12,350 calories as the energy as activation, and assume the ratedetermining process to be governed by collisions between permanganate ions and picric ions, it can be shown that only one activating collision in about 10,000 results in chemical change. (2) An approximate comparison of the number of molecules decomposed with the number of ternary collisions wherein water molecules participate and a heat of activation equal to 15,950 calories is required shows that the efficiency of activating collisions is about one in thirty.4 With the reason for the apparent discrepancy we are not at present concerned. The pertinent conclusion is that there belong to the class of slow bimolecular reactions in aqueous solution chemical changes of a very diversified kind, including the hydrolysis of esters and the breaking of a benzene nucleus.

## Summary.

The kinetics of the reaction between picric acid and potassium permanganate have been studied in aqueous solution. Picric acid is completely oxidised to nitric acid and carbon dioxide; permanganate ions

<sup>&</sup>lt;sup>2</sup> Cf. Moelwyn-Hughes, The Kinetics of Reactions in Solution, p. 200, 1933.

<sup>&</sup>lt;sup>3</sup> La Mer, J. Amer. Chem. Soc., 55, 1739, 1933. <sup>4</sup> Cf. Moelwyn-Hughes and Legard, Trans. Chem. Soc., 424, 1933.

are reduced to manganese dioxide. The reaction is bimolecular over fairly wide ranges of conditions, the constant being independent of the concentration of hydrogen ions, and only very slightly affected by the addition of electrolytes. The absolute velocity is lower than the values calculated by making reasonable assumptions about the type and number of activating collisions. Superficially, the results resemble those found for the hydrolysis of esters, so that slowness of bimolecular reactions in water may characterise chemical changes of a widely different nature.

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THE ABSORPTION OF DYESTUFFS BY CEL-LULOSE. PART I.—THE KINETICS OF THE ABSORPTION OF SKY BLUE FF ON VISCOSE SHEET, IN THE PRESENCE OF VARIOUS AMOUNTS OF SODIUM CHLORIDE.

By S. M. Neale and W. A. Stringfellow.

Received 20th June, 1933.

Any consideration of the process of dyeing by direct dyestuffs, whether from the point of view of the technician or that of the theoretical physical chemist, has up to the present been gravely handicapped by the lack of adequate quantitative data. This is due to the difficulty of preparing these dyestuffs even approximately pure and of estimating accurately the small amounts absorbed. Moreover, the interpretation of the results which are available <sup>1</sup> is complicated by the fact that, when other factors, such as time are investigated, the concentration of dyestuff in the solution is not maintained constant. It is obvious that any consideration of the kinetics of the absorption is rendered very difficult, or indeed almost impossible, if the external concentration is continuously changing as the absorption proceeds.

In the present work on the absorption of dyestuffs by cellulose, such variation has been avoided by the use of a relatively small amount of cellulose, of the order of 10 milligrams. It has been found possible by the use of a new technique to determine quite accurately the amounts of dyestuff, of the order of one-tenth of a milligram, present in such small amounts of material.

Another criticism which applies to almost the whole of the previous work on dyestuff absorption, is that no attempt has been made to separate the effects of rate of absorption and of absorption at equilibrium. Indeed, it is believed that the data now put forward afford the first quantitative proof <sup>2</sup> that a final equilibrium state can be attained in the absorption of a direct dyestuff by cellulose. Moreover, our results show that the absorption of the particular dyestuff studied is a process which can be

 $<sup>^{1}</sup>$  See, for example, Wiktoroff, Koll. Z., 55, 72, 1931; Schramek and Götte, Koll. Beihefte, 34, 218, 1931.

<sup>&</sup>lt;sup>2</sup> Contemporary work leading to a similar conclusion was described by Messrs. Boulton, Delph, Fothergill, and Morton at the June, 1933, Conference of the Textile Institute.

precisely controlled, so that results reproducible within about I per cent. may usually be obtained.

It is proposed to extend the preliminary work described in the present paper so as to study quantitatively the various factors which are known to affect the absorption of direct dyestuffs by cellulose. We intend to examine the effect of the following factors on the absorption of various dyestuffs:-

- (I) Time of dyeing—approach to a final equilibrium.
- (2) Concentration of dyestuff in solution.
- (3) The effect of rising and of falling concentrations. (Reversibility or hysteresis of absorption.)
- (4) Added electrolytes.
- (5) Temperature.
- (6) The condition of the cellulose.

We also propose to investigate the rate of loss of absorbed dyestuff from cellulose immersed in water and in salt solutions, and the rate of diffusion of dyes through cellulose sheet. The results of such a study are necessary in order to provide a sound basis for any speculations as to the mechanism of the process, and may also serve to make possible the quantitative description of the technically important properties of dyestuffs.

The present paper deals chiefly with the effect of the time of dyeing, and of added sodium chloride, the presence of which is essential for the absorption of the particular dyestuff used. The effect of various possible sources of error in the technique which has been evolved is also indicated.

Since one of the primary objects of this initial investigation was the study of the kinetics of the absorption, cellulose sheet prepared by the viscose process was chosen as the absorbent, so as to provide a simple geometrical shape. The soundness of this choice was apparent when it was found possible to treat the kinetics of the absorption as a process of linear diffusion of dyestuff from the surface towards the centre of the

The direct cotton dyestuff known as "Sky Blue FF" (Colour Index No. 518) was chosen for this initial work, on account of its ready solubility, the suitability of its colour for visual estimation, and known chemical constitution. It is prepared by the diazotisation and coupling of I molecule of dianisidine with 2 molecules of the sodium salt of Iamino-8-naphthol-2.4 disulphonic acid, resulting in

Mol. wt. = 992.

The behaviour of other direct dyestuffs is being investigated by other workers in this laboratory, and no exceptions have yet been found to the general principles which arise from the work now described.

## Experimental Materials and Methods.

#### Viscose Sheet.

(a) Specifications.—A large quantity of this material in two thicknessess was obtained from the Cellophane Company in the commercial condition,

containing glycerol. After this had been removed by washing the material had the following properties:—

Mean air dry thickness. 0.00415 cms. (thick). 0.00218 cms. (thin). Fluidity 3 (2 per cent. soln. in cupram- 11.0 (thick), 9.0 (thin). monium). Copper Number (Method of Heyes 4 using 0.76 (thick), 0.69 (thin). carbonate-bicarbonate solution). Dichroic constant 5 when dyed with 0.5 1.35 (thick), 1.55 (thin). per cent. of Benzo-purpurine 4B. (Axis ratio of minimum and maximum absorption of polarised light of wave-length 578  $\mu\mu$ ). Baryta absorption ratio 6 (relative to 3.4 (thick). purified cotton cellulose).

In order to evaluate the apparent diffusion coefficient of the dyestuff in absolute units, it is necessary to know the thickness of the sheet viscose when in the boiling dye solution. The thickness in water has been measured with a micrometer screw gauge and also with an apparatus in which the effects of load and of temperature on the wet thickness could be followed by means of an optical lever. The wet thickness was found to be independent of the temperature between 20° and 100° C., and to be unaffected by the presence of dyestuffs and of sodium chloride in the concentrations used in the dyeing experiments.

(b) Method of Using.—To remove the glycerol present in the commercial product, the Cellophane was first thoroughly washed in distilled water. It was then partially dried between sheets of filter paper under slight pressure so as to avoid crinkling, and finally dried in air at 25° C. The dried sheet was stamped out into small circular discs by means of steel punches.

Discs of the same diameter were found to vary slightly in weight and were therefore rapidly sorted, by weighing them on a sensitive torsion balance into batches in which the weight of each disc was constant to within o·1 mgm. Corrections for moisture content (about 12 per cent.) were made by weighing from time to time a "standard" piece of cellophane, which was exposed to the air of the laboratory.

The "standard" piece and the discs to be used for dyeing experiments were never exposed to temperatures above 25° C.

## Dyestuff.

- (a) Purification.—A sample of Chlorazol Sky Blue FF prepared from purified intermediates, but containing about 30 per cent. of inorganic salts, was supplied by the British Dyestuffs Corporation Ltd. This was purified by twice salting out by means of hot alcohol-sodium acetate mixtures, and washing the final product thoroughly with boiling alcohol. The purified dye was dried for twelve hours in an air oven at 110° C. Under these conditions it still remains approximately I per cent. of moisture.7 In the nearly dry condition such dyes as Sky Blue FF are very hydroscopic, so that precautions must be taken to guard against access of moisture during weighing.
- (b) Criteria of Purity.—It was considered that chemical methods of estimating the purity of the dyestuff were not sufficiently specific, as they

<sup>&</sup>lt;sup>3</sup> Report of the Fabrics Co-Ordinating Research Committee, "The Viscosity of Cellulose Solutions," D.S.I.R., London, 1932.

<sup>&</sup>lt;sup>4</sup> Heyes, J. Soc. Chem. Ind., 47, 90T, 1928. <sup>5</sup> Preston, J. Soc. Dyers and Colourists, 47, 312, 1931. <sup>6</sup> Neale, J. Text. Inst., 22T, 349, 1931. <sup>7</sup> Compare Neale and Hanson, Nature, 129, 761, 1932.

might return isomerides more or less highly coloured than the dye under investigation, or, in the case of titanous chloride, any reducible impurities

which were present.

As criteria of purity, therefore, we made use of (a) the electrical conductivity in aqueous solution at 25° C., which is very sensitive to the presence of inorganic salts, and (b) the "colour-value" of solutions of the dye, determined by means of the Leitz-Duboscq colorimeter, according to the method described under "estimation of dye, etc." It seems reasonable to suppose that the impurities most difficult to separate will be isomerides and homologues of the true dyestuff. These impurities will not be strongly differentiated from the dyestuff in their effect on the result of a chemical analysis, whereas there is a strong probability that their hue and colorimetric value will be distinctive. (A sample of Benzopurpurine 4B, for example, which according to its titanous chloride titre contained 96 per cent. of the pure dye, had a colour-value only 90 per cent. of that of the purest sample available.)

We have found that the colour value of Sky Blue FF solution is independent of the temperature of drying of the dyestuff up to 150° C., of the temperature at which it is dissolved, and of the age of the solution stored in the dark. It is also uninfluenced by the addition of moderate

amounts of salt, acid, or alkali.

The purified specimen used in the present investigation had an equivalent conductivity in 0·15 per cent. solution at 25° C. (corrected for conductivity of water) of 87·1. Specimens prepared by independent workers from a sample of "concentrated" commercial dyestuff obtained from the Sandoz Chemical Co. Ltd., showed a colour value and conductivity identical with that of the sample used in the present work.

# Conditions of Dyeing.

The dyeings were carried out with boiling solutions, contained in Jena resistance-glass tubes, approximately 30 cm. long by 6 cm. in diameter, carrying Jena-glass reflux condensers attached to the tubes by mercury-seal joints.

The cellophane discs, threaded on pure silver wire, in such a manner that they were prevented from touching each other or the walls of the tube, were immersed in the boiling dye solution for a definite time, then quickly removed, rinsed for a moment in cold distilled water, blotted with filter paper, and placed in a known volume of 25 per cent. pyridine-inwater solution, in order to remove the absorbed dye, the amount of which was then determined colorimetrically. The weights of cellophane (i.e., the size and number of discs) and the volumes of the dye baths used were so chosen that the decrease in concentration of the dye solution, except in a few cases, did not exceed 2 per cent. Usually about 10 milligrams of cellophane and about 100 c.c. of dye solution were employed.

# Estimation of Dye Absorbed.

The colorimeter used was made by Messrs. Leitz on the Duboscq principle, in which by means of movable plungers the depths of solution in the paths of two beams of light are adjusted until a uniform field is obtained in an eye-piece. By appropriate choice of volume of the stripping solution the concentration can be made to lie in the optimum range for visual matching, namely from 0.01 to 0.02 grams per litre.

Standard solutions in aqueous pyridine covering this range of concen-

tration were stored in the dark.

Before commencing to use the colorimetric method of estimation, it was proved that the dye solutions obeyed Beer's law over a 3 to 1 concentration range. In subsequent work the concentration-ratio of the solutions under comparison was kept below 2 to 1. In order to improve the conditions of work and to reduce fatigue, the colorimeter was housed in a ventilated

compartment painted white inside. The interior of this could be illuminated with a diffuse blue light, so that the peripheral field of vision was roughly similar in hue and intensity to that seen through the instrument. It was not found helpful to use contrast colour-filters when working with this dye.

For each estimation a number of settings (usually five) were taken, and before each setting, the instrument was re-adjusted for equality of illumination on the two sides. This was done because in our opinion the adjustment for equality of illumination is just as important, and is subject to the same random variations as the setting of the plungers themselves.

With these precautions it was found possible to reproduce results to within less than I per cent., when taking the mean of five settings for each measurement.

## Experimental Results.

Preliminary experiments in which the pure dye was used without added salts, but which were carried out in soft glass vessels, gave irregular results. Conductivity measurements indicated contamination by electrolytes from the glass as a likely explanation. In subsequent experiments apparatus of Jena G glass was employed. It was observed that the amount absorbed in 30 minutes at the boil from a solution containing 1.3 grams of dye per litre but free from added electrolytes was about 0.045 grams per 100 grams of cellulose. Assuming that 100 grams of cellophane occupy 130 c.c. in water at 100° C., it follows that the apparent volume concentration of dye in the cellulose after 30 minutes dyeing is only about one-third as high as in the external solution. In other words, the absorption of this particular dyestuff by viscose sheet is dependent on the presence of some foreign electrolyte. A similar conclusion was reached by Schramek and Götte for certain other direct dyestuffs.

# The Relation between Time of Immersion and Dye Absorption, using Relatively large Amounts of Sodium Chloride.

These experiments represent an approach to the conditions which obtain in technical dyeing, but by the use of small quantities of cellulose only a small fraction of the total dye was absorbed, whereas in technical practice it is usual to exhaust the dyebath as completely as possible.

Tables I. to IX. show the relation between the observed dye absorp-

TABLE I.—ABSORPTION OF SKY BLUE FF BY VISCOSE SHEET ("CELLOPHANE") FROM BOILING AQUEOUS SOLUTIONS CONTAINING SODIUM CHLORIDE.

(Absorption in gms. per 100 gms., dry weights.)

Dye concentration, o·20 g./l.; NaCl concentration, I·0 g./l.; Film weight, 5·7 mgm./cm.²  $D_{\infty}$  taken as o·320 per cent.;  $h/b^2$  as o·51  $\times$  10<sup>-2</sup>; h as 7·5  $\times$  10<sup>-8</sup> cms./min.

Time (Mins.)  Dye absn.	5 0.0675 0.0665		30 0·144	60 60	134 0·254	136 0·260	240 0•304	1050 0·315
obs.	0.0675	0.090	0.146	0.196	_	_	_	0.320
Dye absn. calc	0.059	0.082	0.142	0.198	0.271	0.272	0.307	0.320

# 1172 THE ABSORPTION OF DYESTUFFS BY CELLULOSE

tion, expressed in milligrams of dye per 100 mgm. dry weight of cellophane, and the time of dyeing, for various concentrations of dye and of sodium chloride. Tables I.-III. deal with a fixed salt concentration, 1.0 grams per litre, and dye concentrations from 0.20 to 0.05 grams per litre; in Nos. III.-IX. the dye concentration is the same, while the amount of

#### TABLE II.

Dye concentration, 0·10 g./l.; NaCl concentration, 1·0 g./l.; Film weight,  $5\cdot7$  mgm./cm.<sup>2</sup>  $D_{\infty}$  taken as 0·200 per cent.;  $h/b^2$  as 0·51 × 10<sup>-2</sup>; h as 7·5 × 10<sup>-8</sup> cms./min.

Time (Mins.)	5	10	30	60	120	132	240	255	1050	0.192
Dye absn.	∫0.0424	0.055	0·090	0.0131	0·154	0·159	0·189	0·183	0·203	
	0.429	0.055 0.056	o·090 o·097		0·154 0·156	0.159	o·189 o·184	o·183	0·203 0·199	0·192 0·205

#### TABLE III.

Dye concentration, 0.05 g./l.; NaCl concentration, 1.0 g./l.; Film weight,  $5\cdot7$  mgm./cm²  $D_{\infty}$  taken as 0.125 per cent.;  $k/b^2$  as 0.51  $\times$  10<sup>-2</sup>; k as 7.5  $\times$  10<sup>-8</sup> cms./min.

Time (Mins.) Dye absn. obs. Dye absn.	5	10	30	60	240	380	960
	{0.022	0·034	0·056	0.081	0·120	0·122	0·129
	0.023	0·035	0·054	0.079	0·127	—	0·123
calc	0.023	0.032	0.055	0.078	0.120	0.124	0.125

#### TABLE IV.

Dye concentration, 0.05 g./l.; NaCl concentration, 2.0 g./l.; Film weight, 5.7 mgm./cm. $^2$ 

 $D_{\infty}$  taken as 0.293;  $k/b^2$  as 0.72  $\times$  10<sup>-2</sup>; k as 11.4  $\times$  10<sup>-8</sup> cms./min.

Time (Mins.) Dye absn. obs.	∫0.064	10 0.086 0.087	20 0·125 0·112	30 0·152 0·150	60 0·210 0·220	120 0·265 0·265	240 0·287	420 0·296 0·291	1000 0·293 0·293
Dye absn. calc	0.063	0.088	0.126	0.124	0.311	0.265	0.290	0.293	0.293

#### TABLE V.

Dye concentration, 0·05 g./l.; NaCl, 5·0 g./l.; Film weight, 5·72 mgm./cm.²  $D_{\infty}$  taken as 0·660;  $k/b^2$  as 0·94  $\times$  10 $^{-2}$ ; k as 13·8  $\times$  10 $^{-8}$  cms./min.

Time (Mins.) Dye absn. obs.	5	10	31	60·5	143	240	1000
	{0·173	0·226	0·387	0·528	0·635	0·659	0.660
	0·175	0·228	0·387	0·525	0·632	—	0.653
Dye absn. calc.	0.162	0.226	0.395	0.528	0.640	0.658	0.660

salt is gradually increased to 35.0 grams per litre. Absorption values calculated from diffusion theory, as explained below, are also given in each table.

The data given in Tables IV., V., and VI. are expressed graphically in Fig. 1 by points lying on or near the correspondingly numbered curves, which are not, however, drawn through the experimental points, but represent the calculated variation of dye absorption with time.

#### TABLE VI.

Dye concentration, 0·05 g./l.; NaCl, 12·0 g./l.; Film weight, 5·46 mgm./cm²  $D_{\infty}$  taken as 1·25;  $k/b^2$  as 1·08  $\times$  10<sup>-2</sup>; k as 14·7  $\times$  10<sup>-8</sup> cms./min.

Time (Mins.) Dye absn. obs. Dye absn.	10	30	60	162	166	420	1000
	{0.497	0·764	1·05	1·21	1·18	I·2I	1.30
	{0.478	0·754	1·03	—	—	I·22	1.30
calc.	0.460	0.796	1.04	1.24	1.24	1.25	1.25

#### TABLE VII.

Dye concentration, 0.05 g./l.; NaCl concentration, 20.0 g./l.; Film weight, 5.66 mgm./cm.<sup>2</sup>  $D_{\infty}$  taken as 1.58;  $h/b^2$  as 0.84  $\times$  10<sup>-2</sup>; h as 12.6  $\times$  10<sup>-8</sup> cms./min.

#### TABLE VIII.

Dye concentration, 0.05 g./l.; NaCl concentration, 25.0 g./l.; Film weight, 5.65 mgm./cm.²  $D_{\infty} \text{ taken as 2.00; } h/b^2 \text{ as 0.69} \times \text{10}^{-2}; \text{ $h$ as 10.9} \times \text{10}^{-8} \text{ cms./min.}$ 

Time (Mins.) Dye absn. obs. Dye absn. calc.	10 {0.615 }0.600 0.588	30 0·974 1·03	60 1·39 1·41	233 1·85 — 1·97	241 1·81 — 1·97	1000 2·02 — 2·00
Į						

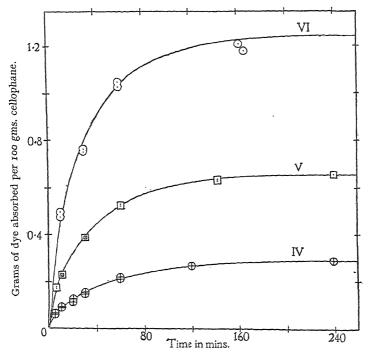
#### TABLE IX.

Dye concentration, 0.05 g./l.; NaCl concentration, 35.0 g./l.; Film weight, 5.65 mgm./cm.²  $D_{\infty}$  taken as 2.58;  $k/b^2$  as 0.53  $\times$  10-2; k as 7.8  $\times$  10-8 cms./min.

Time (Mins.) Dye absn. obs. Dye absn. calc.	10 {0·702 {0·706 0·679	30 1·16 1·17 1·16	60 1·59 1·58	180 2·28 2·23 2·37	1050 2·56 2·59 2·58

# Calculation of Rate of Absorption, from the Theory of Diffusion.

Let us assume that the rate of absorption of the dye by the cellophane is determined, not by a slow chemical reaction, but by a process of simple diffusion which, since the diameter of a disc of cellophane is very large compared to its thickness, may be regarded as occurring only in the direction normal to its surface.<sup>8</sup>



Dye concentration, 0.05 g./l. Curves calculated from diffusion theory. IV. = NaCl, 2.0 g./l. V. = NaCl, 5.0 g./l. VI. = NaCl, 12.0 g./l. Fig. 1.

The amount of dye, dS, which in time dt traverses unit area of an imaginary plane, parallel to the surface of the disc, and distant x cms. from it, will then be given by Fick's diffusion equation:—

$$\frac{\mathrm{d}s}{\mathrm{d}t} = K \cdot \frac{\mathrm{d}c}{\mathrm{d}x},$$

where K is a constant and dc/dx is the concentration gradient of the dye at a point in the plane. If dc/dx were constant, there would be no accumulation of dye at any point during the process. The measure of the rate of accumulation is  $Kd^2c/dx^2$ , so that:—

$$\frac{\mathrm{d}\left(\frac{\mathrm{d}s}{\mathrm{d}x}\right)}{\mathrm{d}t} = \frac{\mathrm{d}c}{\mathrm{d}t} = k\frac{\mathrm{d}^{2}\mathcal{C}}{\mathrm{d}x^{2}}.$$

<sup>8</sup> We do not wish to exclude the possibility that the actual absorption of the dye by cellulose may be due to some form of chemical affinity; our treatment merely assumes that any chemical reaction or absorption is rapid compared with the movement of the dye through the cellulose.

A. V. Hill  $^9$  has made use of this equation as a starting-point in calculations of the diffusion of oxygen into muscle tissue. He finds that in the case of diffusion from both sides, into a plane sheet  $^2b$  cm. thick, the ratio which the amount of diffusible substance absorbed at time  $^t$  minutes from the start bears to the full saturation amount is given by:—

$$\frac{D}{D_{\infty}} = I - \frac{8}{\pi^2} \left( e^{-\frac{k\pi^2t}{4b^2}} + \frac{I}{9} e^{-\frac{9k\pi^2t}{4b^2}} + \frac{I}{25} e^{-\frac{25k\pi^2t}{4b^2}} + \dots \right).$$

The following table gives the theoretically calculated fractional degree of saturation,  $\frac{D}{D_{\infty}}$ , for various values of  $\frac{100 \ kt}{b^2}$ ; (t being reckoned in minutes).

				1				
$\frac{100 \ kt}{b^2}$	0.85	3.12	4.9	7.25	12.2	19.7	28.6	40.4
$D/D_{\infty}$	0.1	0.2	0.25	0.3	0'4	0.2	o·6	0.4
$\frac{\frac{100\ kt}{b^2}}{D/D_{\infty}}$	47·2 0·75	57·0 0·8	84·3 o·9	0.949	135 0·971	0·990 180	225 0·997	

The fact that k and t appear only as a product in the expression for  $D/D_{\infty}$  greatly simplifies the calculation of k, the diffusion constant, from a series of observed values of  $D/D_{\infty}$ . From the table one constructs a curve, or set of curves, from which can be read off the value of  $\frac{100 \text{ }kt}{b^2}$  for any value of  $D/D_{\infty}$ . Taking now the observed values of  $D/D_{\infty}$  for different values of t, under otherwise fixed conditions of dyeing, these standard curves are used to obtain a series of values of t, corresponding to the experimental values of t, and t, are constant, and t, and

Having determined the best representative value for  $k/b^2$ , we make use of it to calculate the values of  $100kt/b^2$  for various experimental times, and read off from our standard curves the corresponding values of  $D/D_{\infty}$ , and thus obtain a series of calculated values of D, the amount of dye absorbed. Values of D so obtained are included in the Tables I. to IX., and have been used in drawing the "theoretical" curves in Fig. 1. The method of calculation used results in an ideal time diffusion curve which most nearly fits the experimental data.

It will be seen from Fig. 1 and Tables III., IV. and V. that, for 0.05 grams of dye and from 1 to 5 grams of salt per litre, the experimental results are very accurately represented by the diffusion equation. For high salt concentrations the agreement with theory is not quite so good, and the results are not so easily reproducible.

The observed values of the absorption for five minutes' dyeing are

<sup>&</sup>lt;sup>9</sup> Proc. Roy. Soc., 104B, 9 pp. 65-70, 1928. (Equation 42 in Hill's paper contains a misprint.)

in almost every case slightly higher than the calculated values. This was probably due to the presence of minute irregularities in the surface. It could not be attributed to a sudden imbition of solvent on putting the cellophane in the dye solution, for a similar result was obtained when the discs were previously boiled for some minutes in water containing salt only, at the same concentration as in the dye-bath, and were then immediately transferred to the latter.

The fact that the diffusion equation satisfactorily represents the increase of absorption with time is not regarded as in itself sufficient proof that the delay in establishing equilibrium arises from slowness of bulk movement of dye through the gel. Curves of the shape observed could conceivably arise from slow chemical reaction or absorption, occurring entirely at or near the surface of the sheet.

# Further Evidence in Favour of the Diffusion Theory.

It has, however, been shown qualitatively, by examining sections under the microscope, that the distribution of the dye in the cellophane-does actually change with time in the manner to be expected from diffusion theory, the colour gradually spreading from the outside towards the centre of the sheet, until it appears to be uniform over the whole section. In order to test this quantitatively, the following experiment was performed. A large piece of cellophane was dyed for 17 hours in a solution containing 5.0 grams of salt and approximately 0.05 grams of dye per litre. About one-quarter of the total thickness was removed from each face of the dyed material by careful scraping. The scrapings, the remaining middle portion, and also a piece of cellophane dyed in the same bath as a control, were then stripped and their dye content determined. The results of two such experiments were:—

		Per Cent.	Dye Content.
Scrapings .		. o·68	0.67
Middle portion		. 0.73	0.65
Control .		. O.7I	0.69

In view of the difficulties of this experiment these figures show that the distribution is at least approximately uniform.

# The Adsorption of Dyestuff by Thinner Viscose Sheet.

If the rate of absorption is in reality determined by a process of diffusion, then the time (t) required to reach a given degree of saturation  $(D/D_{\infty})$  should be proportional to the square of the half thickness (b) of the sheet, so long as the diffusion coefficient (k) remains constant.

We considered, therefore, that the use of cellophane half as thick as that previously employed would afford a valuable check on the diffusion hypothesis, and accordingly carried out a series of dyeings using such material. The results are given in Table X., together with those obtained in a corresponding series of dyeings of the thicker material.

To facilitate comparison the values of  $D/D_{\infty}$ , the fractional saturation, are plotted against corresponding time scales in Fig. 2.

The ratio of the times scales is the square of the ratio of the sheet thickness, in this case  $\left(\frac{5.72}{2.95}\right)^2 = 3.76$ . The fact that the values of  $D/D_{\infty}$  for both thick and thin sheet then lie on or near the same curve, is a valuable confirmation of the diffusion hypothesis and indicates quite.

TABLE X.

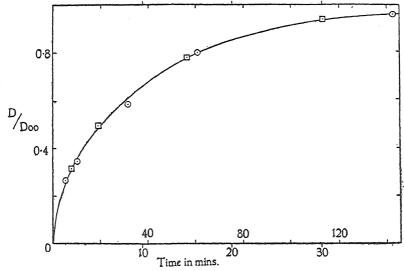
Thin Viscose Sheet (Dry Weight 2.95 mgms./sq. cm.).

Time (Mins.) Dye absorbed per cent.	2 0·236 0·240	5 0·371 0·372	15 0·584 0·584	30 0·692 0·700	60 0·725	150 0.744 0.754
Fractional saturation $D/D_{\infty}$	0.312	0.496	0.780	0.930	0.967	ı

Thick Viscose Sheet (Dry Weight 5.72 mgms./sq. cm.).

Time (Mins.) . Dye absorbed per cent. Fractional saturation $D/D_{\infty}$	5 0·173 0·175	10 0·226 0·228	31 0·387 0·387	60·5 0·528 0·525	143 0.635 0.632	240 0·659 —	1000 0.660 0.653 1.0
·	•	•				) !	

definitely that bulk movement of the dyestuff molecules through the gel is the principal factor determining rate of absorption. The comparison



Thin cellophane.

Dye concentration, 0.05 g./l.

Thick cellophane.

Dye concentration, 0.05 g./l.

Upper scale refers to thick cellophane.

(Ratio of time scales is the square of ratio of thicknesses.)

Fig. 2.—Variation of degree of saturation,  $D/D_{\infty}$ , with time for thick and for thin cellophane.

is, however, not wholly free from objection. The thinner cellophane absorbs more dye at equilibrium and has also been found to swell in water to a less extent than the thicker sheet. A more rigorous check

would evidently be afforded by a comparison of the results obtained with cellophane of the same thickness, when exposed to the dye solution (a) on one side only, and (b) on both sides.

Such an experiment was attempted, and it was found that the amount of dye absorbed at saturation (24 hours) was identical with that taken up when the material was dyed in a similar solution from both sides. On account of experimental difficulties the results for short times of dyeing were, however, not accurately reproducible.

# The Effect of Sodium Chloride on the Equilibrium Absorption and Rate of Diffusion of the Dyestuff.

From the data which have been put forward, it is evident that the addition of salt has a profound effect on the dyeing of the cellophane.

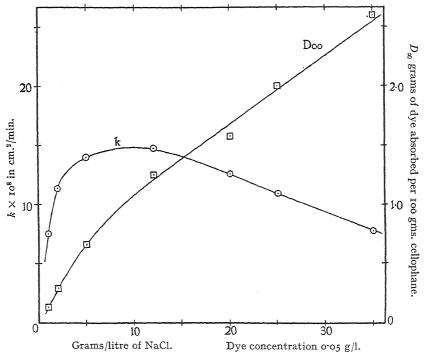


Fig. 3.—Variation of diffusion constant (h), and of saturation absorption  $(D_{\infty})$ , with concentration of sodium chloride.

The available evidence is conveniently summarised in Table XI. and in Fig. 3, by collecting the values of the equilibrium absorption  $(D_{\infty})$  and of the diffusion coefficient (K) for the various concentrations of sodium chloride.

It will be seen that at low concentrations the saturation absorption increases very rapidly, more than in proportion to the concentration of salt, then rises less rapidly, so that a slightly sigmoid curve is obtained. This effect is clearly shown by comparison of the actual figures in Table XI.

The apparent diffusion coefficient, on the other hand, rises rapidly at first with addition of sodium chloride, reaches a maximum between

TABLE XI.

Temperature 101° C.

Dye concentration

					,	,	
Conc. of NaCl grams per litre Absorption at saturation	1	2	5	12	20	25	35
	0.125	0.293	0.660	1.25	1.58	2.00	2.58
min. $\times$ 108)	7.5	11.4	13.8	14.7	12.6	10.9	7.8

5 and 10 grams of salt per litre, and then slowly falls. This behaviour may be contrasted with the effect found by Hartley and Robinson  $^{10}$  for diffusion of dyestuffs in water—that addition of sodium chloride steadily decreases the diffusion coefficient. The order of magnitude of our coefficient for Sky Blue FF in wet cellophane at 101° C., is  $10^{-7}$  cm. $^2$ /min.' whilst Hartley and Robinson find for pure dyestuffs in water a coefficient of the order  $5 \times 10^{-6}$  cms./sec., three thousand times as great.

This is no doubt partly accounted for by the fact that diffusion of the large dyestuff molecules can take place only through faults or open spaces, and not through the cellulose lattice as a whole. Again, the comparatively strong absorption of the dyestuff must in some way reduce its diffusion tendency relative to its total concentration gradient.

We feel that any theoretical speculations regarding the mechanism of the absorption would perhaps be premature. The results which are now put forward show quite definitely that in any explanation of the dyeing of cellulose with direct dyestuffs, the effect of the foreign electrolyte must occupy a position of fundamental importance.

#### Sources of Error.

In connection with such work as we have described, particular attention must be given to the uniformity of the experimental materials. It must be borne in mind that cellulose is not a definite chemical individual, but belongs to the class of high polymers; in its "regenerated" forms, such as cellophane, it might possibly show considerable variations in properties, according to the conditions of manufacture. It was found, however, that cellophane of a given nominal thickness gave very uniform results, both for saturation absorption and also, when slight variations in thickness were allowed for in the calculation, for rate of absorption of dyestuff. Six pieces of cellophane chosen at random from stock without sorting by weight and dyed together for the same time in the same solution, gave, for instance, the figures 0·147, 0·145, 0·143, 0·144, 0·146, 0·144, respectively for the percentage of dye absorbed, at about half saturation.

Solutions of direct cotton dyestuffs are commonly regarded as "colloidal," and, by analogy with other colloids, it might be suspected that their properties would be affected by factors other than their composition, such as thermal history and age. It therefore seems to be desirable to put forward our experience as to the effect of such factors on the absorption of Sky Blue FF by cellulose. It was found, for example, that no change in dyeing properties resulted from:—

(a) Boiling the solutions for 40 hours.

(b) Ageing in the cold for 90 hours and then rapidly heating to the boil before introducing the cellophane.

It is unlikely that adventitious variations in the hydrogen-ion concentration of the dye solution had any appreciable effect upon the absorption. In an experiment in which the  $p_{\rm H}$  was varied from 7.0 to 5.7 by the use of acetic acid sodium acetate buffer mixture, the absorption increased by only 4 per cent.

Small errors may arise from the fact that the temperature of the dye-baths was not under exact control. With increasing temperature the dye is more rapidly absorbed, but  $D_{\infty}$ , the amount taken up at saturation, is smaller—there is a fall of about 4 per cent. in the saturation

absorption per degree temperature rise.

Owing to superheating, the temperature of the boiling solution was actually about 101° C., and probably varied within about 0.5° C. Moreover, the solutions containing 35 grams of salt per litre should theoretically have a boiling-point nearly 0.5° C. higher than those containing 2 grams. No attempt has, however, been made to correct our data for these relatively slight variations of temperature. Experiments are now being carried out under thermostatic control at a series of lower temperatures.

# Summary.

(1) A technique has been devised for accurately measuring the amount of a dyestuff, Sky Blue FF, absorbed by regenerated sheet cellulose, and also for rendering this amount reproducible, under given conditions, within about 2 per cent.

(2) Dyeings have been carried out in the presence of sodium chloride, using various concentrations of salt and of dyestuff, and the effect of such variations upon the rate of absorption and upon the saturation absorption

has been investigated.

(3) The absorption of the dyestuff from pure aqueous solution is negli-

gible, but it increases rapidly with the addition of salts.

(4) It has been found possible to explain the results obtained for rate of absorption in terms of the mathematical theory of diffusion. It is assumed that the outside of the sheet is dyed immediately on immersion, the colour then diffusing towards the centre at a rate proportional to its gradient of concentration in the cellulose phase.

(5) In further agreement with this assumption it is found that cellulose sheet of half the usual thickness dyes to a given fraction of saturation in

one quarter of the time.

(6) The diffusion constant of Sky Blue FF through cellophane immersed in water at 100° C. has been found to be of the order 10-7 cm.²/min. It rises to a maximum and then falls with increasing concentration of salt, but appears to be independent of the concentration of dyestuff within the limits so far investigated.

Our thanks are due to Imperial Chemical Industries Ltd., Dyestuffs Group, for supplying a specially prepared sample of Sky Blue FF, and to Mr. J. Hanson for photo-micrographs of sections of dyed cellophane, and for the measurements of dichroic constants.

College of Technology, Manchester.

# ELECTROPHORESIS OF LECITHIN IN THE PRESENCE OF NEUTRAL SALT; THE DUAL NATURE OF THE CHARGE.

By Christopher Williams Price and W. C. M. Lewis.

Received 24th July, 1933.

In a previous communication  $^1$  an attempt was made, by comparison of lecithin mobility  $p_{\rm H}$  curves, with those of certain simple fats, to obtain some knowledge of the dual nature of the charge on a lecithin dispersion. The dual nature referred to consists (a) of a charge due to the ionisation of the amphoteric groups, and (b) a charge due to adsorption of, presumably, hydroxyl ions on the fatty surfaces of the particles. It was possible at the same time to reconcile the value of the point of reversal of charge, at  $p_{\rm H}=2.7$ , with that of the isoelectric point namely  $p_{\rm H}=5.17$ , as calculated from approximate values of the dissociation constants of lecithin.

In the present work an attempt is made to determine quantitatively the contribution from each of the two sources of electric charge referred to above.

# Experimental.

As before, the lecithin was extracted from fresh egg yolks and purified by the method of Levene and Rolf.<sup>2</sup>. The material was kept in a dark desiccator under dry nitrogen and used when in the stable condition.

The apparatus and the method of determining the electrophoretic mobility of the dispersions follows that recently described by the writers.

Measurements were carried out with various electrolytes e.g., aluminium chloride, thorium chloride and barium chloride. Of these aluminium chloride and thorium chloride were found to be unsuitable since it was desirable to use citrate buffer with which aluminium and thorium form complex anions. In any case their application is restricted to  $p_{\rm H}$  values < 4. Only the barium chloride results are recorded in the present paper.

0.05 per cent. aqueous dispersions of lecithin together with the requisite concentration of barium chloride were buffered with N/100 citrate buffer. The supernatant solution had the same ionic concentration. The  $p_{\rm H}$  of this solution agreed to 0.01 of a  $p_{\rm H}$  unit with that of the dispersion. The addition of 2 per cent. sucrose to the dispersion was found again to facilitate greatly the adjustment and maintenance of a sharp boundary without affecting the mobility in any way, in accordance with experiments of Northrop and Cullen. With this artifice no difficulty in the maintenance of a sharp boundary was experienced for the concentrations of barium chloride used in the present work.

The values of the velocities obtained in cm./sec. were corrected to

<sup>&</sup>lt;sup>1</sup> Price and Lewis, Trans. Faraday Soc., 29, 775, 1933.

<sup>&</sup>lt;sup>2</sup> Levene and Rolf, J. Biol. Chem., 72, 587, 1927. <sup>3</sup> Northrop and Cullen, J. Gen. Physiol, 4, 635, 1921-22.

20° C. by multiplying by the factor  $\eta_{x^{\circ}}/\eta_{20^{\circ}}$  where  $\eta_{z^{\circ}}$  and  $\eta_{20^{\circ}}$  are respectively, the viscosities of water \* at the temperature of measurement and at 20° C.

The  $p_{\rm H}$  values below  $p_{\rm H}=7$  were measured by the gold quinhydrone electrode (Corran and Lewis),<sup>4</sup> for higher values of  $p_{\rm H}$ , the glass electrode (Harrison) 5 was used.

TABLE I. (The sign denotes the sign of the charge.)

Concentration of $BaCl_2 = 0.025N$ .	Concentration of $BaCl_2 = 0.03N$ .			
$p_{\rm H}$ Values. $v \times 10^5$ .	$p_{\rm H}$ Values. $v \times 10^{8}$ .			
2·39 + II·9 3·60 + 4·15 4·7 Isoelectric point (interpolated value).  4·90 - 0·64 5·29 - I·69 6·63 - 4·60	2·36			
Concentration of $BaCl_2 = 0.034N$ .	Concentration of $BaCl_2 = 0.04N$ .			
$p_{\rm H}$ Values. $v \times 10^5$ .	$p_{\rm H}$ Values. $v \times 10^5$ .			
2·38 + 8·25 3·23 + 4·85 3·58 + 2·6 4·80 + 0·2 5·1 Isoelectric point (interpolated value). 5·29 - 0·4 6·45 - 2·1	2·38 + 7·7 3·17 + 4·7 3·58 + 2·6 4·80 + 0·45 5·1 Isoelectric point (interpolated value).  5·29 - 0·4 6·00 - 1·25			
7·8i — 3·95	7·08 — 2·75 7·37 — 3·4			

Concentration of	of $BaCl_2 = 0.15N$ .
$p_{ m H}$ Values.	$v \times 10^5$ .
2.48	+ 8.7
3.52	+ 6.3
4.16	+ 5.95
4.44	+ 5.1
4.76	+ 4.25
5.12	+ 3.4
6.55	+ 3.4
8.97	+ 3.1

A representative record of an electrophoretic mobility determination is given.

<sup>\*</sup> The ratio  $\eta x^{o}/\eta 20^{o}$ , for the solutions used, is not sensibly different from that of water at the same temperature.

4 Corran and Lewis, Biochem. J., 18, 1358, 1924.

<sup>&</sup>lt;sup>5</sup> Harrison, J. Chem. Soc., p. 1528, 1930.

Composition of dispersion: o·o5 per cent. lecithin; 2 per cent. sucrose; o·o1N citrate buffer; o·o3N BaCl<sub>2</sub>.

 $p_{\rm H} = 3.21$ .

Potential gradient = 2.82 volt/cm.

Temperature = 20° C. Current = 9.0 milliamps.

Movement of Boundary.					
Cathode Limb.	Time				
(Upwards).	(Mins.).				
0	0				
2°0	10				
4°0	20				
6°0	30				
	Cathode Limb. (Upwards).  0 2:0 4:0				

Mean movement=6·0 scale divisions in 30 mins. (I scale division = 0·043 cm.). Electrophoretic mobility under a potential gradient of I volt/cm. at 20°  $C.=5\cdot08\times 10^{-5}$  cm./sec.

Table I. shows the variation of the electrophoretic mobility of 0.05 per cent. dispersions of lecithin at various concentrations of barium chloride. In general the symbol v stands for the mobility in cm./sec. under a potential gradient of I volt/cm. at 20° C.

#### Discussion.

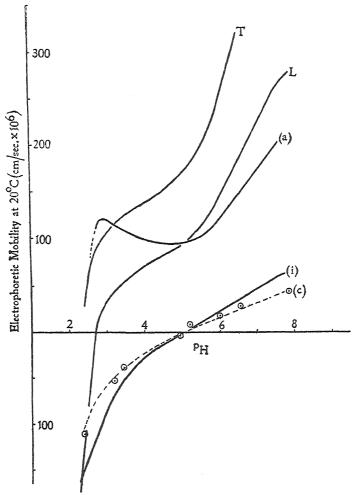
From a consideration of Table I. and the curves in Fig. 1, it will be observed that at a concentration of barium chloride of 0.025N the point of reversal of charge has shifted from  $p_{\rm H}=2.7$  to  $p_{\rm H}=4.7$ . On increasing the concentration of barium chloride to 0.03N this point is shifted further towards the alkaline region, viz., to  $p_{\rm H}=5.1$ . On further increasing the concentration to 0.034N and again to 0.04N no change in the position of the point of reversal of charge takes place, but the mobility  $p_{\rm H}$  curve revolves around this point to give, on both the positive and negative sides, a lesser value of the mobility. It will be demonstrated that this change in the value of the mobility may, with certain assumptions, be accounted for by regarding lecithin in the presence of the above concentrations of salt as a simple amphoteric body free of its adsorption charge.

It will be observed also that for comparatively high concentrations of barium chloride (e.g., 0.15N), barium ions are adsorbed in excess of that required just to neutralise the adsorption charge, and the dispersion becomes positively charged at all  $p_{\rm H}$  values. Above  $p_{\rm H}=5\cdot 1$  the mobility is independent of the  $p_{\rm H}$ . Below this point there is an increase in the value of the mobility due, presumably, to a superimposed charge from the ionisation of the amino members of the amphoteric groups.

The point of reversal of charge in the presence of 0.03N (or 0.04N) barium chloride, corresponds almost exactly to the isoelectric point calculated from approximate values of the dissociation constants of the amphoteric groups of lecithin, *i.e.*,  $p_{\rm H} = 5.17$  (v. Price and Lewis 1). The assumption is made therefore, that at the above concentrations of barium chloride the adsorption portion of the charge has been com-

pletely nullified and we can look upon the lecithin as behaving simply as an amphoteric body in the presence of neutral salt.

H. A. Abramson 6 assumes that for proteins, at a given  $p_{\rm H}$  value the mobility v depends simply upon  $\kappa$  the reciprocal of the thickness



In o o IN citrate buffer.  $\begin{cases} T = \text{Tristearin (observed)}. \quad L = \text{Lecithin (observed)}. \\ (a) = \text{Adsorption charge (deduced)}. \end{cases}$  (i) = Ionisation charge (deduced). (i) = Ionisation charge (deduced). (ii) = Ionisation charge (deduced). (iii) = Ionisation charge (de

of the double layer. This is distinct from the behaviour of "inert" surfaces (e.g., oil emulsions) for which v may vary with the surface charge density  $\sigma$  or with  $\kappa$  or with both. That is, in the case of proteins  $\sigma$  remains constant if the  $p_H$  is fixed; (it is postulated that any varia-

<sup>&</sup>lt;sup>6</sup> H. A. Abramson, J. Gen. Physiol, 16, 592, 1933.

tion in  $\sigma$  due to  $\kappa$  varying is very small compared with explicit variation of  $\kappa$ ).

From the Debye-Hückel and Helmoltz-Smoluchowski equations Abramson 7 derives the equation

$$Q = C\pi\eta vr(\kappa r + 1).$$

Substituting the values of the various constants he obtains

$$Q = C\pi\eta vr \left[ (r\sqrt{\mu} \times 3.3 \times 10^7) + 1 \right] \qquad . \tag{1}$$

where  $\mu = \frac{1}{2} \sum n_i Z_i^2$  is the ionic strength of the solution, C is a constant Q the charge on the particle, and r its radius.

As a closer approximation to the observed behaviour Abramson uses an empirical form of the above equation, viz.:

$$Q = C\pi\eta vr(\kappa r + 2\cdot 4)$$

for the particular case of a uni-univalent electrolyte which does not shift the isoelectric point, e.g., gelatine in acetate buffer. On the assumption that Q is constant at a given  $p_{\mathbb{H}}$  he then finds that the ratio

$$\frac{v_1}{v} = \frac{\kappa r + 2\cdot 4}{\kappa' r + 2\cdot 4}$$

agrees well with the observed values. Here,  $v_1$  and  $\kappa_1$  refer to the appropriate values in N/500 and v and  $\kappa$  in N/50 salt concentration.

In the present case we may look upon the lecithin particles in the presence of sufficient barium chloride as owing their charge simply to their amphoteric groups. We also make the assumption that Q for a given value of  $p_{\mathbb{H}}$ , is constant in such a case.

The value of r for lecithin is probably of the order of 1 to  $5 \times 10^{-5}$  cm.  $\sqrt{\mu}$  is of the order of unity. Consequently the term unity in equation (1) may be neglected and we have

$$\frac{v_1}{v} = \sqrt{\frac{\mu}{\mu_1}},$$

i.e., v varies inversely as the square root of the ionic strength of the solution.

For two of the salt concentrations used, 0.03N barium chloride and 0.04N barium chloride in citrate buffer we thus obtain

$$\frac{v_1}{v} = 1.09.$$

In Fig. 1 the mobility  $p_{\rm H}$  curve calculated for lecithin in the presence of 0.03N barium chloride from data observed in 0.04N barium chloride, is shown as a dotted line (curve c). The observed data for 0.03N barium are plotted as open circles. The agreement is excellent.

A similar calculation is made in order to obtain the mobility  $p_{\rm H}$  relationship for the hypothetical amphoteric body in the presence of 0.01N citrate buffer. Here

$$\frac{v_2}{v_1} = 1.55$$

where  $v_2$  is the mobility in citrate buffer and  $v_1$  that in 0.03N barium chloride and citrate buffer. The curve calculated for lecithin free of its adsorption charge, in 0.01N citrate is shown in Fig. 1 as curve i.

<sup>7</sup> H. A. Abramson, J. Gen. Physiol., 15, 575, 1932.

If we take this calculated curve to represent the electrophoretic behaviour of lecithin under the above hypothetical conditions, we are at once in the position to resolve the net charge, \* on a lecithin dispersion in OOIN citrate buffer, into its two components, viz.: the charge due to adsorption and that due to ionisation (of the amphoteric groups)

respectively. These are shown in Fig. I as curves a and i.

It is of interest to compare the mobility  $p_{\rm H}$  curve of the adsorption charge component with that of tristearin. From this comparison it is evident that both the slope of the curve and the individual values of the mobility are of a definitely higher order in the latter case. the earlier paper the writers pointed out that during the formation of the dispersion (at  $p_{\rm H}=6.8$  in the absence of buffer) the influence of the amphoteric groups upon the adsorption charge is such that the particles do not adsorb hydroxyl ions to nearly the same extent as a simple fat free from ionisable groups, would do. This would account for the above difference.

Again, below  $p_{\rm H}=5\cdot 1$  to at least  $p_{\rm H}=2\cdot 8$ , the adsorption charge curve (Fig. 1, curve (a)) rises as the  $p_{\rm H}$  falls. This is contrary to the direction followed by the corresponding curve of a body (e.g., tristearin) whose charge is independent of any ionisable groups. This behaviour in part was to be expected from a comparison of the mobility  $p_{\rm H}$  curves of lecithin and certain non-ionising fats (v. Price and Lewis).\frac{1}{} The more or less obvious suggestion was made that "the presence of positively charged ionised groups tends to repel hydrogen ions from the surfaces of the particles and consequently to decrease their discharging efficiency upon the fatty part of the surface." But this is not the same thing, however, as requiring an actual increase in effective adsorption charge with decrease in  $p_{\rm H}$ . The present examination has brought to light a new point, viz.: that the repulsion of hydrogen ions, as a consequence of the presence of positively charged amphoteric groups elsewhere in the unit, is so notable that the discharging, or neutralising, efficiency of the hydrogen ions upon the fatty part of the surface is even less at say  $p_{\rm H}=3$  than it is at  $p_{\rm H}=5.^{+}$  It is clear that it is only at  $p_{\rm H}=5.1-5.2$ that the adsorption charge is undisturbed by the amphoteric groups.

\* Strictly speaking the & potential. However, since we have corrected for changes in  $\kappa$  and have both the hypothetical ionisation curve and the true lecithin curve under the same conditions, we have effectively  $\kappa$  and presumably  $\kappa r$  constant. This being so, we are making a true comparison of the charges. By way of illustration equation (1) has been used to calculate the charge at a few  $p_{\rm H}$  values. r is taken as 5  $\times$  10  $^{-5}$  cm. The results are as follows:—

<i>р</i> <sub>н</sub> .	Ionisation Charge.	Adsorption Charge.	Total Net Charge.
	(E.S.U.)	(E.S.U.)	(E.S.U.)
5°1	0	- 11·1 × 10 <sup>-5</sup> 0 - 13·7 × 10 <sup>-5</sup> - 13·9 - 23·2 ,	- 11·1 × 10 <sup>-5</sup>
2°3	+ 18·6 × 10 <sup>-5</sup>		+ 18·6 ,,
2°73	+ 13·7 ,,		0
2°8	+ 12·3 ,,		- 1·6 × 10 <sup>-5</sup>
7°5	- 6·9 ,,		- 30·1 ,,

While the values for the ionisation charge are probably correct, it is doubtful if equation (1) holds for the adsorption charge.

† Alternatively, since we must look upon the phenomenon as a reversible one, that hydrogen ions already binding adsorbed OH ions are repelled from the sphere of their influence by the increasing positive charge emanating from the amphoteric groups.

One point now remaining is the existence of a maximum at about  $p_{\rm H}=2.8$  in the adsorption curve (a). That this curve cannot rise indefinitely in the acid region, is evident from the fact that the ionisation charge curve (i) cuts the observed lecithin curve at  $p_{\rm H}=2.3$ . At this point the adsorption charge must be zero, in the presence of citrate buffer alone.

This behaviour was to be expected since the very great increase in hydrogen ion concentration (represented by a small lowering of  $p_{\rm H}$  in this region) must eventually have a swamping effect upon any influence the amphoteric groups might have on the discharging efficiency of these hydrogen ions.

The lecithin dispersion is of interest as being the first case in which charges due to ionisation and charges due to adsorption, present simultaneously, though at different positions on one and the same dispersed unit, are capable of being estimated individually.\* The importance

$$\left(\frac{v_1}{v} \text{ (calc.)} = \frac{\kappa v + I}{\kappa_1 v + I} = I \cdot 37; \frac{v_1}{v} \text{ (obs.)} = I \cdot 3\right).$$

of the behaviour exhibited by lecithin lies in the conclusion that the presence of amphoteric groups has an appreciable effect upon the magnitude of the adsorption of ions on the purely fatty portions of the surface of the unit. Perhaps the most striking consequence of this influence is the existence of a minimum in the purely adsorption charge at the  $p_{\rm H}$  which corresponds to the isoelectric point of the amphoteric groups, followed by a maximum at a lower  $p_{\rm H}$  value.

# Summary.

1. It has been shown that a lecithin dispersion with the addition of not too great a concentration of barium chloride, may be regarded as a dispersion of a simple amphoteric body, free of its adsorption charge.

2. The isoelectric point of lecithin under these conditions is found to

agree with the value calculated by Price and Lewis.

3. The effect of varying the concentration of barium chloride from 0.03N to 0.04N has been calculated from the formula

$$\frac{v_1}{v} = \sqrt{\frac{\mu}{\mu_1}} = 1.09$$

and found to agree with the observed data.

- 4. An attempt has been made to separate the net charge on a lecithin dispersion (in the presence of 0.01N citrate) into its two parts, viz, the charge due to ionisation of the amphoteric groups and that due to adsorption of negative ions at the fatty surfaces of the particles. It has
- \* Tiselius (Roy. Soc. Sci. (Upsala). Series IV., Vol. 7, No. 4) has observed the effect of barium ions upon the mobility of egg albumin. The effect is very small. He finds for instance that the isoelectric point is shifted from  $p_{\rm H}=4.55$  to 4.63 by the use of 0.02N barium acetate in place of 0.02N sodium acetate. A similar addition of barium ions in the case of lecithin shifts the isoelectric point from  $p_{\rm H}=2.7$  to about 4.7, a relatively enormous shift. We might conclude from this that any adsorption of OH-ions on the surfaces of the protein particles is extremely small, but we cannot altogether deny the possibility of its existence. We might in fact suggest that the value of the isoelectric point in 0.02N barium acetate, namely 4.63, is nearer to the true point of neutrality of the amphoteric groups than is the value 4.55. This has support from the fact that the change in the slope of the mobility  $p_{\rm H}$  curve due to the presence of barium ions, observed by Tiselius, may be accounted for more or less quantitatively by the effect of the addition of this concentration of barium ions upon the thickness of the double layer (v. Abramson).

been shown that the adsorption charge passes through a minimum at the

isoelectric point of the amphoteric groupings.

It should be emphasised that the total number of negative ions adsorbed on the fatty surface has been assumed to remain constant throughout. The minimum in the adsorption change simply indicates that the number of these negative ions which are effective for electrophoresis is a minimum at the point referred to.

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# ON THE EVAPORATION AND DIFFUSION OF VOLATILE MATERIALS INTO AN INERT GAS STREAM.

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The true mechanism of the problem of evaporation from a liquid surface still appears to be but imperfectly understood, and the present short paper is an attempt to correlate the various results of other workers in this field, and if possible, to clarify a little the position.

It is a fact that the well-known Herz-Knudsen equation :-

$$m=p.\sqrt{\frac{M}{2\pi RT}}$$

in which m, is the "ideal" rate of evaporation in grams per square centimetre per second,

p, is the vapour pressure in mm. Hg.
M, is the molecular weight of the vapour,
T, is the absolute temperature of evaporation,
and R, is the gas constant in appropriate units,

gives results for the value of m, very greatly in excess of the actual rates of evaporation measured under particular physical conditions at normal pressures, when calculated from the known value of the vapour tension p, at absolute temperature T. At the outset it must be recognised, however, that this value of m, obtained from the Herz-Knudsen equation is the ideal rate of evaporation in vacuo, for the formula represents the rate of striking of a surface by a vapour obeying the gas laws, and thus the interchange of molecules between the two phases when the liquid is in equilibrium with its vapour. For the realisation of this ideal rate it is essential that all vapour molecules leaving the liquid surface are at once removed by some means, say condensation, from the sphere of action.

It is instructive to review first the work which has been done on the influence of adsorbed insoluble monomolecular oil films upon the evaporation of water. At first G. Hedestrand 1 concluded that the presence of such oil films did not affect the measured rate of evaporation at 20°, although later it was shown 2 that at lower pressures than atmospheric the actual rate of evaporation was markedly lowered by such films. Hedestrand's measured rate of evaporation at normal pressures was only 0.0025 per cent. of the ideal rate. N. K. Adam 3 employing an air streaming method, obtained a rate of evaporation from a clean water surface at 18° of only 1 × 10<sup>-7</sup> gms./cm.<sup>2</sup>/sec., but observed that the issuing air was almost saturated with water vapour, and concluded that the limiting factor in the observed rate of evaporation was the capacity of the air to remove the water vapour; a fact no doubt tacitly realised by all workers. In a like manner, R. P. Bell 4 working on the evaporation of chlorine from its water solution, found that under similar conditions the rate of evaporation of chlorine was proportional to the concentration of the gas in solution. A calculation shows that for the higher chlorine concentration, the partial pressure of chlorine in the issuing gas was approximately 0.1 mm. Hg., the measured rate of evaporation being only about I per cent. of the ideal rate. Bell found also that reductions up to 15 per cent. in the rate of evaporation were obtained by the addition of tri-chloracetic acid. In this connection it is interesting to note that the rates of evaporation of sodium oxide from pure soda-silica glasses heated under identical conditions were approximately proportional to the concentration of Na<sub>2</sub>O up to a certain limiting constitution of the glasses.<sup>5</sup>

That it is possible to realise the Herz-Knudsen rate of evaporation has been shown for metal filaments heated in high vacua, particularly for the metals cadmium and zinc.<sup>6</sup> Experiments showed close agreement between the vapour tensions determined by a study of the rates of evaporation and those obtained by dynamic methods involving the formation of saturated vapours. Early experiments on mercury vapour <sup>7</sup> also received confirmation, <sup>8</sup> and more recently similar determinations on platinum and molybdenum, <sup>9</sup> silver, iron, copper and nickel <sup>10</sup> have shown the correctness of the theory.

Departures from the theoretical rates of evaporation when experiments are conducted in vacuo, are undoubtedly to be explained by the physical conditions of the determinations. Thus, working on a somewhat larger scale, A. A. Sunier <sup>11</sup> carried out a series of experiments on the evaporation of cadmium from the molten metal in high vacua, but employed a mass of material of some 615 grams of metal. For the sixty determinations made, the average rates of evaporation were about 10 to 15 per cent. of the ideal rates, on one occasion in the range 35 to 40 per cent. Whilst his results showed many factors to be outside experimental control, they indicate that the Herz-Knudsen equation

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    J. Physic. Chem., 28, 1245, 1924.
    E. K. Rideal, ibid., 29, 1585, 1925; I. Langmuir, ibid., 31, 1719, 1927.
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    L. Preston and W. E. S. Turner, J. Soc. Glass Tech., 16, 331, 1932.
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    I. Langmuir and G. M. J. Mackay, Physic. Rev., 4, 377, 1914.
    H. A. Jones, I. Langmuir and G. M. J. Mackay, ibid., 30, 201, 1927.
    J. Physic. Chem., 32, 1516, 1928.
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does actually represent the rate of interchange between liquid and vapour in a state of equilibrium.

Further to this point, A. Claassen and C. F. Veenemans 12 have investigated the evaporation of the heavy earths, barium, strontium and calcium oxides, in vacuo at temperatures up to 1800° Abs. Their results showed a linear relationship between log  $(m\sqrt{T})$ , and I/T, that is, the value of  $m\sqrt{T}$  followed a vapour pressure form, and, although the authors do not say so, since m, the rate of evaporation is given from the Herz-Knudsen equation by:-

$$p = m\sqrt{T} \cdot \frac{17\cdot 14}{\sqrt{M}}$$

this means that whatever fraction of the ideal rate was realised then this fraction was appreciably constant. This fraction or "accomodation coefficient" 13 the authors have assumed to be unity, and gave vapour tension formulæ of the usual type from which can be obtained the result that barium oxide, the most volatile of the three, has a vapour tension of 33 × 10 - 6 mm. Hg., at 1008°, indicating as is well known the extreme stability of these oxides.14

Sunier attributed his low results mainly to a dirty evaporating surface, 15 a film of cadmium oxide, but it appears certain that the efficiency of the condensing system was of some influence. Moreover, it appears to the present writer that in any experimental procedure, such as that of Sunier and Claassen and Veenemans, involving the condensation of the evaporated molecules on a surface not far removed from the evaporating surface itself, then there must exist a pressure gradient or concentration gradient of molecules across the intervening space. This being so, it would be unreasonable to expect to be able to measure the ideal rate of evaporation by measurements of the amount of condensed material.

At this stage it is not inappropriate to consider the following simple calculation for the evaporation of water at normal pressures. Let us assume a water surface of one square centimetre in a tube of two centimetres diameter through which nitrogen is passed at the rate of 10 c.c. per minute (measured at N.T.P.), the total pressure of the system being maintained at 760 mm. Hg.16 Let the further assumption be allowed that as the nitrogen passes over the surface it becomes saturated with water vapour, so that, if the experiment be carried out at 20° the partial

 $^{12}$  Z. Physik, 80, 342, 1933.  $^{13}$  A term suggested by Knudsen.  $^{14}$  Quite recently, S. Miyamoto (Trans. Faraday Soc., 29, 794, 1933) has put forward a theory of the rate of sublimation, in which, by an elaboration of Langmuir's theory by the application of Maxwell's distribution law of velocities for a gaseous system, the "accommodation coefficient"  $\alpha$  of the Herz-Knudsen coefficient is deduced to be: equation is deduced to be:

$$\alpha = e^{-\frac{Mu_0^2}{2RT}}$$

if it be assumed that amongst the molecules of the gas which collide with the solid surface, only those having components of velocities at right angles to the interface greater than a threshold value  $u_0$  are able to condense on the solid surface. In which case  $\alpha$  can only be unity when  $u_0$  is zero.

<sup>15</sup> A similar effect had previously been noted for mercury, vide R. S. Mulliken and W. D. Harkins, J. Amer. Chem. Soc., 44, 37, 1922, and M. Knudsen, Ann.

Physik, 47, 697, 1915.

16 Conditions closely agreeing with those of the apparatus of E. Preston and

W. E. S. Turner, loc. cit.5

pressure of water vapour in the issuing gas will be 17·15 mm. Hg. To realise this we shall require a rate of evaporation of water of only  $3.2 \times 10^{-6}$  grams per second. If now this value be substituted in the Herz-Knudsen equation (an act for which there is no justification), we should obtain a vapour tension of only  $298 \times 10^{-6}$  mm. Hg., an impossible result for the correct value is 17.54 mm. Hg. It is, of course, obvious how the rate of evaporation will be dependent upon the rate of flow of nitrogen provided that our preliminary assumption is fulfilled; for to obtain a result which will give the true vapour tension in the equation we should require a rate of nitrogen flow 58,900 times greater than that with which we have carried out the above calculation, corresponding to a gas velocity through the tube of some 66 miles per hour.

Experimental tests might well show that our assumed rate of flow is too small for such a relatively high vapour tension to prevent diffusion of the water vapour against the oncoming nitrogen stream; but whatever the minimum rate of flow, the amount of water vapour required to saturate the gas will be independent of the water surface exposed. It appears then that the application of the Herz-Knudsen equation to such circumstances would have no meaning. However, in the dynamic determination of vapour tensions, from a study of which this paper is one result, it is found that saturation of the inert gas never occurs, and the experimentally determined vapour tensions have to be extrapolated back to zero rate of flow of the inert gas to obtain the true vapour tension. This fact does not invalidate the preceding argument, neither does it alter the conclusion that there is no direct connection between the Herz-Knudsen equation and the evaporation from a liquid surface under such conditions.

# Diffusion and the Dynamic Determination of Vapour Tensions.

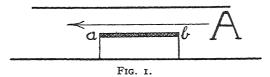
The dependence upon diffusion of the observed rates of evaporation into a gas stream has been commented on. The problem is a complex one and does not as yet appear to have been the subject of analysis. Indeed, the diffusion of one gas into another in a closed system in which there is no movement of the gases as a whole, is of a complexity such that theoretical considerations can lead to quite contradictory conclusions. This latter problem has received a good deal of mathematical analysis, <sup>17</sup> and in the following pages some of the conclusions have been utilised by the present writer in an endeavour to demonstrate that there is some unknown connection between the Herz-Knudsen equation, representing the rate of striking of a given surface by a vapour obeying the gas laws, the process of diffusion, and the observed rates of evaporation into a stream of inert gas.

In the literature the writer has been unable to find any series of results adaptable to his purpose, and has therefore turned to the results published by Professor Turner and himself on the dynamic determination of the vapour tensions of the oxides PbO, Na<sub>2</sub>O and K<sub>2</sub>O <sup>18</sup> from molten glasses at high temperatures. Whilst the precision of these experiments is not high, it is believed that the results represent true vapour tensions, at least within an accuracy of  $\pm$  10 per cent.

The apparatus employed has been described elsewhere 5 and, putting

Notably by Einstein, Clerk Maxwell, E. Meyer, J. H. Jeans, G. Gross,
 Stefan, L. Boltzmann and D. Enskog.
 E. Preston and W. E. S. Turner, J. Soc. Glass Tech., 16, 219 and 331, 1932.

the conclusions before the argument, Fig. 1, is believed to represent an idealised view of the processes taking place. Into an inert gas stream A, volatile material (shown cross-hatched) from the glass surface is attempting to establish its partial pressure by diffusing into the passing gas. The writer has finally been led to regard the degree of saturation

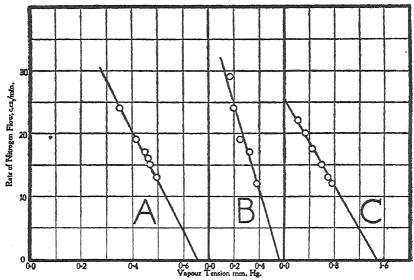


in the issuing gas stream as indicative of the rate of diffusion into the gas stream. In what precise manner this degree of saturation is dependent upon the diffusion coefficient is unknown. It will, among other things, be dependent upon the rate of nitrogen flow, and it is unlikely that the relationship will be linear. Nevertheless, defining the degree of saturation as:—

the vapour tension determined at any rate of flow the extrapolated value at zero rate of flow,

considerations of this ratio lead to interesting results in conjunction with the Herz-Knudsen equation.

Fig. 2 shows the graphs of the results of the vapour tension measurements by a dynamic method for glasses of the approximate compositions:



 $A = PbO-SiO_2$  glass.  $B = Na_2O-SiO_2$  glass.  $C = K_2O-SiO_2$  glass. Fig. 2.—Vapour tensions at 1200° of the volatilising oxides, PbO,  $K_2O$ ,  $Na_2O$ .

30 per cent. PbO, 70 per cent.  $SiO_2$ ; 50 per cent.  $Na_2O$ , 50 per cent.  $SiO_2$ ; and 50 per cent.,  $K_2O$ , 50 per cent.  $SiO_2$ . The assumption is now made that at any moment the vapour of the volatilising material just outside the liquid surface, that is, over a distance comparable with mole-

cular dimensions, is in dynamic equilibrium with the liquid phase, corresponding with the cross-hatched layer of Fig. 1. On this assumption the rate of exchange of molecules between liquid and vapour is given by the Herz-Knudsen equation. If we further regard the concentration of vapour molecules as uniform throughout the infinitesimal section, the equation will also give us the rate of impact of these vapour molecules against that portion of the wall of the gas stream denoted on Fig. 1, by a-b. Regarding the physical conditions of the experiments, the graphs of Fig. 2 are all for 1200°, the values of the total pressure of the system for the several determinations varying between 745 and 765 mm. Hg., so that the results for this purpose are regarded as all being obtained at the same temperature and pressure. The rate of nitrogen flow was in all cases measured at N.T.P., the actual values of the rate of flow over the glasses contained in special platinum semi-cylindrical containers, placed in a platinum tube and heated to the required temperature, being, of course, much higher than this due to thermal expansion of the nitrogen, they will however, be constant at constant temperature and pressure.

From the Herz-Knudsen equation we have that the number of molecules impacting per second is proportional to

$$\frac{m}{M} = p \cdot \frac{\sqrt{\frac{M}{2\pi RT}}}{M} = \frac{C}{\sqrt{M}} \cdot p \text{ if } T \text{ is constant.}$$

In Table I., figures are given showing the degree of saturation, as defined above, for the three glasses at rates of nitrogen flow of 20, 15, and 10 c.c. per minute respectively. In the column headed H-K number, are figures proportional to the number of molecules impacting in unit time, obtained by dividing the true vapour tension p, by the square root of the molecular weight.

TABLE I.—Values of the Degree of Saturation and Number of Molecules Impacting in Unit Time (H–K number), for the three Glasses at 1200°.

Degree of Saturation at Rates of Nitrogen Flow of		Glass.	"H-K number"	
c.c. per minute.			$\sqrt{M}$	
0·66 0·50 0·24	0·75 0·62 0·44	0.83 0.75 0.61	PbO-SiO <sub>3</sub> Na <sub>2</sub> O-SiO <sub>2</sub> K <sub>2</sub> O-SiO <sub>2</sub>	0·043 0·071 0·143

These values are shown plotted in Fig. 3. The relationship between the degree of saturation and the number of molecules impacting in unit time on a given area, is seen to be practically linear, irrespective of molecular type. Further it is apparent from this presentation that the degree of saturation is decreased as the number of impacting is increased. This result is indeed striking, but it can be shown that in the diffusion of a given number of one kind of molecule into another given number of the same kind (Maxwell's "diffusion of a gas into itself"), then D, the diffusion constant, giving the number of mole-

cules diffusing through unit cross-section in unit time is given by: 18

$$D = k \cdot \frac{\eta}{M \cdot (c + c')}$$

in which c' is the concentration of the first group of molecules ("marked molecules").

c is the concentration of the molecules into which those represented by c' are diffusing ("unmarked molecules"), M is the molecular weight, the same for c and c',

 $\eta$  is the viscosity of the gas,

and k is a numerical constant.

In this hypothetical case it is seen that the number of molecules diffusing is inversely proportional to the total concentration.

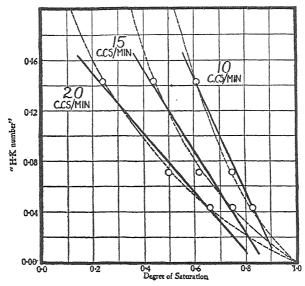


Fig. 3.—Relationship between "H-K number" and degree of saturation for the three glasses at 1200°.

Again, a rigorous investigation by D. Enskog <sup>20</sup> on the inter-diffusion of dissimilar molecules, has shown the diffusion coefficient to be, to a first approximation,

$$D = \frac{3\sqrt{RT}}{32\sqrt{2\pi}N_{A}\psi}\sqrt{\frac{M+M'}{MM'}}\frac{1}{c+c''}$$

where  $\psi$  depends upon the law of force between the molecules and in the case of elastic spheres  $=\frac{(d+d')^2}{16}$  and at constant temperature this reduces to:

$$D = k \cdot \sqrt{\frac{M + M'}{MM'}} \frac{1}{c + c'}$$

<sup>&</sup>lt;sup>19</sup> Vide K. F. Herzfeld and H. M. Smallwood, H. S. Taylor's "Treatise on Physical Chemistry," 2nd Ed., Vol. I., 210.
<sup>20</sup> Physikal Z., 12, 533, 1911.

Again, the diffusion coefficient is seen to be inversely proportional to the total concentration. Now, if c remains constant, and c' be increased, the value of D will then decrease in a manner similar to the simple equation:

$$D = \frac{k}{a + x}$$

where k and a are constants.

Whilst these formulæ are only strictly applicable to cases for isolated systems of gases at rest to their surroundings, i.e., the interchange and interdiffusion of two gases in a closed box, it would be very doubtful to apply them to our practical case of diffusion into a gas stream. It is, however, interesting to view the results of Fig. 3, in the light of these equations. It has been assumed that the degree of saturation is some function of the diffusion coefficient D, and the graphs show that the numerical value of this function decreases with increasing number of impacting molecules, which we will now call c', whilst the number of nitrogen molecules passing in unit time remains constant at the value c. This has been shown to be theoretically the case for two gases under somewhat different circumstances. There is still the problem of the different molecular weights. It will be noted that in the Enskog equation quoted above, there occurs the factor:

$$\sqrt{rac{M+M'}{MM'}}$$

the value of which only changes slightly for the three different values of M', as is shown in Table II.

From the above table it appears that TABLE II.—DIFFUSION OF PbO, this factor will only be of slight importance. Accordingly, the broken curves of Fig. 3 are drawn as portions of curves of the type:

$$x = \frac{a}{a+y}$$

for positive values of y. The relationship between the number of impacting molecules and the degree of saturation

K2O AND Na2O IN NITROGEN.

Oxide.	Molecular Weight M'.	$\sqrt{\frac{M+M'}{MM'}}$ .
PbO	223	0·20I
K <sub>2</sub> O	96	0·214
Na <sub>2</sub> O	62	0·227

It is difficult for the present writer at least, to interpret this resultany more closely than this. There may now be considered cases in which the total number of molecules of both kinds varies, that is, c and c' both vary. In order to do this resource has been had to the complete results for the soda-

then appears to be of the form corresponding to the Enskog equation.

silica glasses 21 over the temperature range 1100° to 1350°, and for the lead oxide containing glasses over the range 1150° to 1350°.22 In this case, a different rate of flow of nitrogen is chosen at each different temperature, so that, in unit time, with increasing temperature a decreasing number of nitrogen molecules passes over the surface of the glasses. In a similar manner to Fig. 3, the degree of saturation values have plottedbeen against the H-K numbers (now divided by the factor

<sup>&</sup>lt;sup>21</sup> E. Preston and W. E. S. Turner, J. Soc. Glass Tech., 16, 331, 1932. 22 Ibid., 219.

 $\sqrt{T}$ , obtained in a like manner to Table I. These results are shown for the soda-silica glasses in Table III., and Fig. 4.

TABLE III.—Values of the Degree of Saturation and the Number of Molecules Impacting in Unit Time, with Varying Rates of Nitrogen Flow for the 50 per cent. Soda-Silica Glass.

Temperature.	Rate of Nitrogen Flow, c.c./min. N.T.P.	Degree of Saturation.	"H-K number" $= \frac{p}{\sqrt{MT}}.$
1100°	20	0·375	0.0007
1200°	15	0·63	0.0018
1300°	10	0·70	0.0043
1350°	5	0·84	0.0068

The approximate representation is hyperbolic. The fact that the degree of saturation increases with increasing number of impacting molecules is not a contradiction of the previous statement, for now the nitrogen concentration is varying, and as the concentration of nitrogen molecules will be far greater than that of the volatilising material, it is to be noted from Table III., that for the first three rates of flow, namely, 20 to 10 c.c. per minute, the degree of saturation is

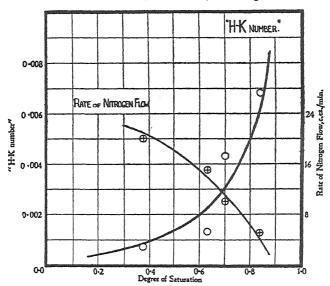


Fig. 4.—Relationships between, degree of saturation, "H-K number," and rate of nitrogen flow, for the soda-silica glass, 1100°-1350°.

very approximately inversely proportional to the concentration of nitrogen molecules. For the rate of flow of 5 c.c. per minute, it would appear that the number of impacting molecules per second has become comparable with the number of nitrogen molecules passing over the surface in the same time.

Similarly, Table IV. and Fig. 5 contain the data for the 30 per cent. lead oxide containing glass.

TABLE IV.—Values of the Degree of Saturation and the Number of Molecules Impacting in Unit Time, with Varying Rates of Nitrogen Flow, for the 30 per cent. PbO Glass.

Temperature.	Rate of Nitrogen Flow, c.c./min., N.T.P.	Degree of Saturation.	"H-K number" $= \frac{p}{\sqrt{MT}}.$
1150°	25	0·5	0.0006
1200°	20	0·66	0.0012
1250°	15	0·75	0.0021
1300°	10	0·76	0.0045
1350°	5	0·87	0.0065

Again an approximate representation of the results is given by a hyperbolic form of curve.

In these two cases we should correctly consider the temperature coefficient of diffusion. From Enskog's equation it will be seen that

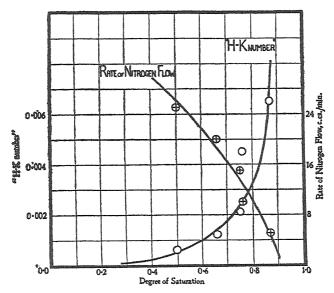


Fig. 5.—Relationships between degree of saturation "H-K number" and rate of nitrogen flow for the PbO-SiO<sub>2</sub> glass, 1150°-1350°.

the factor  $\sqrt{RT}$  occurs, so that with other conditions constant, the diffusion coefficient should vary in a linear manner with the square root of the absolute temperature. This value will only vary from  $\sqrt{1373}=37$ , to  $\sqrt{1623}=40$ , over the range of temperature studied and therefore it has been ignored.

#### Conclusion.

It is concluded therefore, that evaporation at normal pressures whilst ultimately governed by the rate of flow of gas over the evaporating surface, is in essence a process by which a thin vapour or "super surface" layer, in equilibrium with the liquid phase according to the Herz-Knudsen

equation, diffuses into the passing gas. This diffusion appears to be sensibly governed by the same considerations as those deduced from the kinetic theory for the diffusion of gases in an enclosed space. Furthermore, it appears correct to assume that the vapour molecules of PbO, Na<sub>2</sub>O and K<sub>2</sub>O are unimolecular, for otherwise there would be no relationship of the type shown in Fig. 3.

And lastly, the writer wishes to record here his grateful thanks to Professor W. E. S. Turner, of the Department of Glass Technology,

Sheffield, for his continued interest and advice.

The Department of Glass Technology, The University, Sheffield.

# THE EFFECT OF HYDROGEN-ION CONCENTRA-TION ON THE CORROSION OF IRON.

By J. M. BRYAN, Ph.D.

Received 26th July, 1933.

This work is part of a programme of research undertaken by the Food Investigation Board on the corrosion of tin-plate by food products.

Apart from the highly controlled quantitative work of Bengough and his colleagues, much research on corrosion has been semi-quantitative, conducted in open vessels with no control of the gaseous phase. The present work has been carried out in a closed system designed to imitate conditions within a food container. The experiments and their interpretation are limited to a particular class of steel corroded under certain specified conditions.

# Methods and Apparatus.

These were the same as those described in a previous paper on the corrosion of tin.<sup>1</sup> The hydrogen-ion concentration of the corroding medium (5 gm. of citric acid per litre) was varied, as before, by buffering with sodium citrate. The volume of the corroding liquid was 180 c.c. and the headspace was 60 c.c. in each case. The metal, a mild steel, such as is used in the manufacture of tin-plate, was of the following composition:<sup>2</sup>

Carbon combined, 0.07 per cent.; uncombined carbon, very slight trace; phosphorus, 0.05-0.06 per cent.; sulphur, 0.05-0.06 per cent.;

manganese, 0.38 per cent.; silicon, 0.01 per cent. or trace.

The specimens, measuring 3 ins.  $\times$  1 in. and about  $\frac{1}{100}$  in. in thickness, were abraded with emery cloth to remove the film of oxide and smooth the edges, washed in boiling absolute alcohol, dried and placed in a desiccator. The units, containing the prepared specimens partially immersed in the corroding liquid, were maintained at a uniform temperature of 25° C. for a period of 4 days unless otherwise stated. There was no complication due to an insoluble phase since the products of corrosion remained in solution, hence the loss in the weight of the strips was taken

J. M. Bryan, Trans. Faraday Soc., 27, 607, 1931.
 Messrs. Melingriffiths, tin-plate manufacturers of Cardiff, kindly supplied the specimens of steel with its analysis.

as a measure of the corrosion. Unfortunately, specimens from the same batch of steel, but from different sheets, were found to vary in relative corrodability, so that it was necessary to take specimens from the same sheet to obtain consistent and comparable results. The sheets of metal chosen may be regarded as being of a relatively slow corroding type. Most of the measurements were made in quadruplicate, but five or six units were taken in certain tests to decide a point of particular importance. Much better agreement between similarly treated specimens was obtained with tin in the previous work than with steel, which suggests that the differences in the present investigation were related to chemical or physical variations in the metal and not to variations in external conditions.

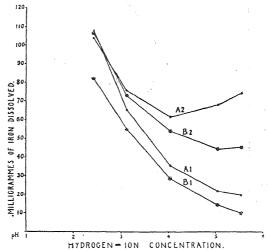
### Experimental.

## I. The Effect of Variation of Hydrogen-ion Concentration for two Types of Surface.

Since it is well known that the corrosion of iron is influenced considerably by the condition of the metallic surface, the effect on corrosion of coarse abrasion as against fine abrasion, over a  $p_{\rm H}$ -range, both in the presence and absence of air, was investigated.

1. In the Absence of Air.—Two sets of strips were prepared which differed only in the surface treatment of the metal. One set, subse-

quently referred to as "smooth having a surface, was abraded with Oakey's "FF" emery cloth and finished with "O" Hubert emery paper; the other, in which the surface is regarded as being "rough" was treated with the "FF" grade only. Oxygen was eliminated from the corrosion bottles and solutions by boiling in vacuo according to the method described previously.4 The corrosion vessels were attached to graduated that the burettes so progress of corrosion evolution of hydrogen. The loss in weight of the strips is recorded by curves AI and BI of



could be followed by Fig. 1.—The effect of surface treatment on the corobserving the rate of rosion of steel, in the presence and absence of evolution of hydrogen.

The loss in weight of A= Rough surface.

The seffect of surface treatment on the corrosion of steel, in the presence and absence of oxygen, at different hydrogen-ion concentrations.

A= Rough surface.

2 = Air present.

Fig. 1, which show that the effect of a rough, as compared with a relatively smooth surface, is to increase the rate of corrosion over the whole  $p_{\mathbf{H}}$ -range. The curves of Fig. 2 record the progressive differences between the evolution of hydrogen from rough and smooth surfaces at different  $p_{\mathbf{H}}$ -values, and show that the effect of a rough surface is actually more marked initially at low, than at high acidity, but subsequently is noticeably the greatest at  $p_{\mathbf{H}}$  2.4. These curves intersect in such a manner that their order is finally reversed.

I = Air absent.

<sup>4</sup> Trans. Faraday Soc., 27, 609, 1931.

<sup>&</sup>lt;sup>3</sup> F. N. Speller, Corrosion—Causes and Prevention, p. 74, 1926.

In the more acid members of the series the attack was mostly confined to the edges, initially, but subsequently extended towards the middle regions and became fairly general over the whole surface of the strips. In the less acid members of the series corrosion was mostly confined to the middle regions, the edges being less attacked. Traces of oxygen were found to have a pronounced effect in inducing this distribution of corrosion (see p. ). When special precautions were taken to eliminate oxygen from the units, the attack was fairly general over the whole surface of all the strips, but there remained a tendency for corrosion to be more concentrated at the edges with increasing acidity.

2. In the Presence of a Limited Supply of Air. —Two further sets of strips were prepared, as before, but were immersed in corroding solutions containing dissolved air; 70 c.c. of air was also present in the headspace of the bottles and gas-burettes. Curves A2 and B2 of Fig. 1 show that the effect of surface differences is negligible at  $p_{\rm H}$  2.4, but the wide

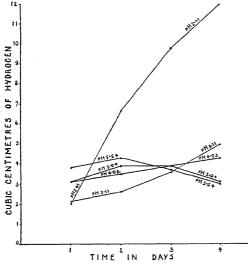


FIG. 2.—Progressive differences, over a period of 4 days, between the evolution of hydrogen from rough and smooth steel surfaces, respectively, at various hydrogen-ion concentrations, in the absence of air.

divergence towards the less acid end of the  $p_{\rm H}$ -scale gives evidence of a marked increase in corrosion at low acidity due to the rougher surface.

The residual gases were analysed to determine the evolution of hydrogen and absorption of oxygen and the results are shown in Fig. 3. Curves E and F show that the absorption of oxygen increases with decreasing acidity. Curves A, B, C and D show that, even when oxygen is present, the curve for the evolution of hydrogen is roughly parallel with the curve for corrosion and that the hydrogen-evolution type of corrosion is considerably stimulated by a rough surface at low acidity. The discrepancy

between the volume of hydrogen evolved and the hydrogen-equivalent of the metal dissolved is due partly to solution of hydrogen in the liquid, but mainly to its combination with oxygen. There is also evidence that some hydrogen was absorbed by the metal and rubber tubing. It is not possible to forecast the amount of this discrepancy unless the solutions are analysed for ferric iron after the test, since at the more acid end of the series the dissolved iron is mainly in the ferrous condition, while at the less acid end enough ferric iron is present to colour the solutions. We may, however, regard the difference between the two pairs of curves (curves A and C and curves B and D) as representing approximately the amount of corrosion occurring through combination of oxygen with hydrogen, and it is seen that this is much the same with both types of surface at all acidities.

The following conclusions may be drawn from an inspection of the

<sup>&</sup>lt;sup>5</sup> Trans. Faraday Soc., 27, 611, 1931.

curves of Fig. 1. (1) Oxygen greatly increases the corrosion in the least acid members of the series and its influence declines rapidly with increasing acidity. (2) In the most acid members of the series  $(p_{\rm H} 2.4)$  corrosion is much the same over a given period whether oxygen is present or not. This is true in all cases, although it is least evident in curve B1, representing corrosion with a smooth surface in the absence of air.

II. The Effect of Variation of Hydrogen-ion Concentration in the Presence of a Limited Supply of Air for Different Periods of Immersion.

When oxygen was present it was not possible to follow the progress of corrosion by daily readings of the burettes, since the increase in volume due to evolution of hydrogen was masked by absorption of oxygen. The rate of corrosion could only be followed by varying the period of immersion. Experiments were carried out, therefore, with specimens abraded alike with Oakey's "FF" emery cloth and immersed for periods of 1, 4 and 7 days respectively.

The results are recorded by the curves of Fig. 4, and show that the form of the curve depends largely upon the duration of the tests,

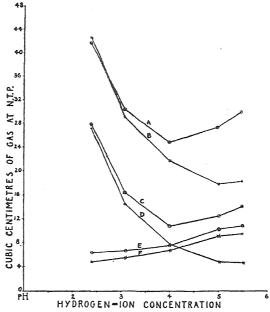


Fig. 3.—Curves comparing the hydrogen found by analysis after a corrosion test with the hydrogen-equivalent of the iron dissolved.

A = Hydrogen-equivalent of iron dissolved (rough surface).

B = Hydrogen-equivalent of iron dissolved (smooth surface).

C = Hydrogen found by analysis (rough surface). D = Hydrogen found by analysis (smooth surface).

E = Absorption of oxygen (rough surface).

F = Absorption of oxygen (smooth surface).

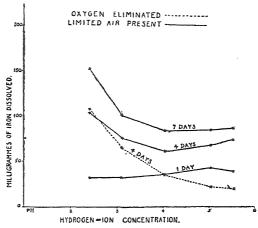


Fig. 4.—The corrosion of steel in the presence of a limited amount of air (with a curve showing the corrosion in the absence of air for comparison).

Table I. records the volumes of hydrogen evolved and oxygen absorbed after r and 4 days.

TABLE I THE VOLUMES OF HYDROGEN	EVOLVED AND OF OXYGEN ABSORBED
DURING CORROSION IN THE	Presence of Air.

$p_{ m H}$	Volume of	Hydrogen	Volume of Oxygen		
	Evolved	I (in c.c.).	Absorbed (in c.c.).		
of Solutions.	After	After	After	After	
	One Day.	Four Days.	One Day.	Four Days.	
2·41	5.7	27·9	0·9	6·3	
3·11	5.7	16·3	I·2	6·5	
4·03	7.2	10·8	I·9	7·5	
5·04	9.5	12·4	2·4	10·2	
5·54	8.6	14·0	2·3	10·8	

The figures show that the absorption of oxygen increased with decreasing acidity and there is no doubt that this is mainly because a reduction in acidity accelerates the rate of formation of ferric iron (see

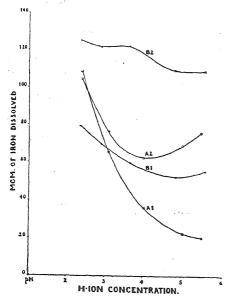


Fig. 5.—The effect of ferric citrate in solution on the corrosion of steel in the presence and absence of oxygen, at different hydrogen-ion concentrations.

A = No ferric iron initially present.
B = Ferric iron initially present.

I = Air absent.

2 = Air present.

p. 1208). The evolution of hydrogen was greater initially at low than at high acidity, although it was ultimately much the greatest at  $p_{\rm H}$  2·4.

At  $p_{\rm H}$  2·4 and 3·1 the edges suffered most attack, but at  $p_{\rm H}$  5·0 and 5·5 the reverse was the case, a zone at the edges being comparatively free from attack and the central regions corroded. At  $p_{\rm H}$  4 the type of corrosion was transitional between the other two. The attack was particularly severe at the surface of the liquid; this was obviously due to the presence of oxygen as the effect was unobserved in its absence.

# III. The Effect of the Addition of a Ferric Salt to Solutions of Different Hydrogen-ion Concentration.

The previous studies showed that the effect of oxygen on corrosion increased with increasing  $p_{\rm H}$ . It seemed desirable to continue this investigation and ascertain (I) whether the observed effect of

oxygen was connected with the formation of ferric iron, since it was found that the rate of oxidation of ferrous to ferric iron increased greatly with decreasing acidity, and (2) how far the efficiency of ferric iron as a depolariser of hydrogen was influenced by  $p_{\rm H}$ .

The effect of ferric iron was studied in the presence and absence of air, so as to determine the combined effect of oxygen and ferric iron. The conditions of the experiment differed only from previous ones in the following respects. The total capacity of the bottles was 280 c.c. and the volume of solution was 220 c.c. The corroding media were buffered as previously but contained in addition 0.5 gm. of ferric iron (freshly prepared in the form of citrate) per litre of solution. As a result of the addition of the ferric iron the  $p_{\rm H}$ -range became 2.38, 2.93, 3.68, 4.88 and 5.65.

I. In the Absence of Air.—The nitrogen used to replace air from the solutions and headspace of the bottles was freed from oxygen by the method of Kautsky and Thiele. The bottles were attached to gas-burettes so that the evolution of hydrogen could be followed and blank tests were set up with no metal test pieces so that the burette readings could be corrected for the absorption of nitrogen. A little strong solution of potassium hydroxide was placed in each burette to absorb carbon dioxide liberated through the breakdown of

through the breakdown of some oxidation product of the citric acid (see p. 1206). The results for corrosion are given by curve B1 of Fig. 5. Curve A1 represents the amount of corrosion in the absence of added ferric iron and is reproduced from Fig. 1 for comparison. These curves show that ferric iron inhibits corrosion at the more acid end of the  $p_{\rm H}$ -range and accelerates it at  $p_{\rm H}$ -values > 3.

Fig. 6 records the progress in the evolution of hydrogen. The general form of curves  $p_{\rm H}$  2·38, 2·93 and 3·68 is the same as that normally encountered with solutions containing no ferric iron, being almost linear except for the initial lag probably due to rapid reduction of the ferric iron at this acidity. At  $p_{\rm H}$  4·88 and 5·65 reduction of the ferric iron is visibly slower than at higher acidities. It is interesting to observe

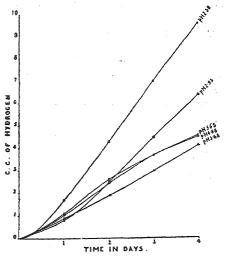


Fig. 6.—The progress of the corrosion of steel in the presence of ferric iron and absence of air, as shown by the production of hydrogen, on successive days, at different hydrogen-ion concentrations.

It is interesting to observe that the evolution of hydrogen is initially greater at low than at high acidity, a result which agrees with that obtained for corrosion in the presence of air (see Table I. and discussion).

The amount of ferric iron reduced during corrosion (see Table II.) was calculated from the quantity found in the solutions by titrating with titanium chloride after the test.

From the data presented by curve Br of Fig. 5, the curves of Fig. 6 and the figures of Table II., we can render an account of the reactions in terms of hydrogen (see Table III.). The figures show that there is a slight difference between the hydrogen-equivalent of the metal dissolved and the sum of the hydrogen evolved and that used in the reduction of ferric iron. This is due mainly (a) to solution of hydrogen in the corroding medium, and (b) to reduction of a portion of the ferric iron by citric acid. That (b) preponderates in the less acid members of the series is proved by the

<sup>&</sup>lt;sup>6</sup> H. Kautsky and H. Thiele, Z. anorg. Chem., 152, 342, 1926.

$p_{_{ m H}}$ of Solutions.	2*38.	2.93.	3.68.	4.88.	5.65.
Amount of Ferric Iron Originally Present in Solution (in gm.) .	0.1065	0.1064	0.1066	0.1054	0.1073
Amount of Residual Ferric Iron (in gm.)	0.0078	0.0067	0.0114	0.0144	0.0098
Amount of Ferric Iron Reduced (in gm.)	0.0987	0.0997	0.0952	0.0910	0.0972

TABLE II .- THE AMOUNT OF FERRIC IRON REDUCED DURING CORROSION.

negative values shown in columns 4 and 5 of the table. Depolarisation of hydrogen by ferric iron was responsible for much the greater part of the corrosion over the whole  $p_{\rm H}$ -range.

TABLE III.—An Analysis of the Reactions in Terms of Hydrogen.

$p_{_{ m H}}$ of Solutions.	2.38.	2.93.	3.68.	4.88.	5.65.
(A) Hydrogen-equivalent of the Iron Dissolved (in c.c.)	31.7	27.9	23.7	20.8	22.0
(B) Hydrogen-equivalent of the Ferric Iron Reduced (in c.c.)	19.7	19.9	19.0	18.2	19.5
Reduced (in c.c.)	9.7	6.4	4.1	4.2	4.6
B+C	29•4	26.3	23.1	22.7	24.1
Difference $A - (B + C)$	2.3	1.6	0.6	-1.9	-2·I

2. In the Presence of a Limited Supply of Air.—The solutions were identical in composition with those used previously but were not freed from oxygen. The volume of air was 90 c.c. as against 70 c.c. in Experiment 1 (2), otherwise the two tests were comparable.

The figures for corrosion are shown by curve B2 of Fig. 5; curve A2 of the same figure is reproduced from Fig. 1 for comparison and shows the amount of corrosion in the absence of added ferric iron. The curve for corrosion in the presence of ferric iron and oxygen together (curve B2) is roughly parallel with the curve for corrosion in the presence of ferric iron without air present (curve B1), but there is a noticeable inflection in the middle region (see discussion).

A marked difference was observed in the situation of corroded areas in the more acid and less acid members of the series. At  $p_{\rm H}$  2·38, 2·93 and 3·68 the upper portion was severely corroded, the lower part being relatively unattacked; at  $p_{\rm H}$  4·88 and 5·65 the reverse was true. Corrosion at the edges was more severe at high than at low acidity, whether air was present or absent. In general, the effect of air was to concentrate the attack at the edges. There was pronounced corrosion at the surface of the liquid especially at the lower acidities.

The amounts of ferric iron reduced during corrosion and the changes in the gaseous phase were estimated as before, and the results are recorded in Table IV.

Table IV. shows that (a) the amounts of hydrogen evolved were small relatively to the total corrosion, (b) the volumes of oxygen absorbed and

TABLE IV.—THE AMOUNTS OF HYDROGEN EVOLVED, OXYGEN ABSORBED AND FERRIC IRON REDUCED DURING CORROSION IN THE PRESENCE OF AIR AND FERRIC IRON.

$p_{ m H}$ of Solutions.	2.38.	2.93.	3.68.	4.88.	5.65.
Volume of Hydrogen Evolved (in c.c.)	12.7	8•4	5.9	5.0	5.2
Volume of Oxygen Absorbed (in c.c.)	6.4	8· <sub>5</sub>	11.4	13.6	14.7
Amount of Ferric Iron Reduced during Corrosion (in gm.) .	0.1004	0.0987	0.0956	0.0907	0.0895

the final amounts of ferric iron present increased progressively with increasing  $p_{\rm H}$ .

A balance sheet of corrosion in terms of hydrogen is shown below in Table V.

TABLE V.—An Analysis of Corrosion in Terms of Hydrogen.

$p_{ m H}$ of Solutions.	2*38.	2.93.	3.68.	4.88.	5.65.
(A) Hydrogen-equivalent of the Iron Dissolved (in c.c.) (from curve B2 of Fig. 6).	50.1	48.4	48.6	43.3	43.1
(B) Sum of the Hydrogen-equivalent of the Ferric Iron Reduced and the Volume of Hydrogen Evolved (in c.c.) (from the data of Table IV.)	32.8	28.1	25.0	23.1	23.1
(C) Difference (A - B)	7.7.0	20.3	23.6	20.2	20.0

The difference (C) between the hydrogen-equivalent of the metal dissolved and the sum of the hydrogen evolved and that used in the reduction of ferric iron is due mainly to the combination of this gas with oxygen (depolarisation). Taking into consideration the figures for the absorption of oxygen (see Table IV.), it is observed (see Table VI. below), that a considerable discrepancy exists between these figures, expressed in terms of hydrogen, and those in Table V. (C).

Table VI.—Comparison between the Volumes of Oxygen actually Absorbed during Corrosion, in Terms of Hydrogen, and those Calculated from the Figures of Table V.

$p_{ m H}$ of Solutions.		2.38.	2*93.	3.68.	4.88.	5.65.
(A) Figures from Table V. (C)		17:3	20.3	23.6	20.2	20.0
(B) Hydrogen-equivalent of the of Oxygen Absorbed (in c.c.)	Volum	12·8	17.0	22.8	27.2	29.4
Discrepancy $(A - B)$		4.2	3.3	0.8	-7.0	-9.4

The discrepancy at the more acid end of the  $p_H$ -range is accounted for, to some extent, by solution of hydrogen in the corroding medium and,

possibly, by adsorption of this gas by the metal and rubber tubing. The high negative values in the last two columns prove that considerable amounts of oxygen are used in the induced oxidation of the citric acid at low acidity, a result which confirmed previous work.<sup>7</sup> The volumes

TABLE VII.—The Increase in the Volumes of Hydrogen Evolved and Depolarised due to the Single Effect of Oxygen.

$p_{ m H}$ of Solutions.	2.38.	2.93.	3.68.	4.88.	5.65.
(A) Increase in the Hydrogen-equivalent of the Metal Dissolved due to the Single Effect of Oxygen (in c.c.)	18.4	20.5	24.9	22.5	21.1
(B) Increase in the Volume of Hydrogen Evolved due to the Single Effect of Oxygen (in c.c.)	3.0	2.0	1.8	0.2	0.6
(C) Volume of Hydrogen Depolarised by Oxygen (in c.c.) (A - B)	15.4	18.5	23.1	22.0	20.5

of oxygen absorbed during corrosion, therefore, are not those actually used in the kathodic depolarisation of hydrogen. The latter, however, can be calculated by substracting the figures in (B) from the corresponding

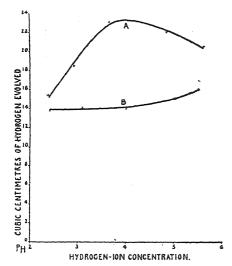


Fig. 7.—A comparison of the volumes of hydrogen depolarised by oxygen in the presence and absence of added ferric iron.

B = No ferric iron initially present in solution.

A = Ferric iron initially present in solu-

ones in (A) of Table VII. This table is based on Tables III. and V., *i.e.*, on the results of experiments on the corrosion of iron by ferric citrate in which the presence of air was the only difference.

From this we see that the effect of oxygen on the corrosion of iron in the presence of ferric citrate is (1) to stimulate slightly the evolution of hydrogen, and (2) to depolarise or combine with hydrogen on the surface of the metal.

Table VII. shows that, when ferric iron is present in solution, the maximum effect of oxygen on corrosion occurs in the neighbourhood of  $p_{\rm H}$  4, and is due mainly to depolarisation which is responsible for the inflection observed in curve B2 of Fig. 5.

It is of value to compare the volumes of hydrogen depolarised by oxygen as set out in (C) of Table VII. with those obtained for the parallel experiment in the presence of air but with no added ferric iron in

solution. This comparison is seen in Fig. 7 in which Curve A represents the volumes of hydrogen depolarised by oxygen when ferric iron is initially present, and curve B the amounts depolarised under similar condi-

<sup>&</sup>lt;sup>7</sup> Trans. Faraday Soc., 29, 833, 1933.

tions but with no added ferric iron in solution (curve B represents the difference between curves A and C of Fig. 3). The difference between these two curves (Fig. 7) gives an approximation of the amounts of hydrogen depolarised indirectly through the action of the added iron as an oxygen-carrier. This action is at its maximum at a hydrogen-ion concentration of about  $p_{\rm H}$  4, a result which serves to throw further light on the cause of the inflection of curve B2 of Fig. 5.

The main results of this investigation are summarised as follows:—(I) If the corrosion in the absence of air and ferric iron is taken as a base, it is found that ferric iron causes a slight inhibition of corrosion in the more acid members of the series and accelerates it in the less acid members. (2) Oxygen causes a pronounced acceleration in the rate of corrosion over the whole  $p_{\rm H}$  range studied, when ferric iron is present initially in solution. (3) In the presence of ferric iron most of the hydrogen is removed through depolarisation, irrespective of  $p_{\rm H}$  or the presence or absence of oxygen. (4) When ferric iron is present initially, free oxygen has a maximum effect on corrosion at about  $p_{\rm H}$  4, which is due mainly to depolarisation of hydrogen. (5) There is evidence that part of the depolarisation of hydrogen by oxygen is brought about by the action of iron in solution as an oxygen-carrier, especially at about  $p_{\rm H}$  4.

### Discussion.

The results for the corrosion of iron in the absence of air, as given by curves AI and BI of Fig. I, are in general agreement with those of Shipley and his co-workers.<sup>8</sup> These curves, although roughly parallel, diverge somewhat at either end. Fig. 2 reveals that the divergence at the more acid end of the series is a secondary effect. Initially, at high acidity, the corrosion was confined mainly to the edges of the strips, but subsequently developed over the whole of the surface; it might be expected therefore, that those strips with the rougher surface would, as a secondary effect, corrode more quickly than those with the smoother surface. This spreading of the corroded area from the edges towards the middle regions, at high acidity, may be attributed to the stirring effect of the evolution of hydrogen, which disrupts the liquid film at the surface of the metal where concentration differences are likely to exist. The divergence of curves AI and BI of Fig. I, at the less acid end of the series, is an initial effect and may be attributed to the more even distribution of corrosion over the whole surface of the strips at low acidity; hence differences in the surface of the metal might be expected to have the greatest effect at this end of the  $p_{\rm H}$  range, initially, and less effect as corrosion proceeded.

The divergence of curves A2 and B2 of Fig. I showing the corrosion in the presence of air proves that the effect of surface differences increased progressively with decreasing acidity. The curves of Fig. 3 clearly show that the rougher surface encourages the hydrogen-evolution type of corrosion at low acidity, notwithstanding the fact that oxygen was present. Examination of the specimens showed that oxygen accentuated the corrosion at the edges in the more acid members of the series and protected them in the less acid members. Surface differences would therefore have little or no effect on the rate of corrosion at the more

<sup>&</sup>lt;sup>8</sup> J. W. Shipley, I. R. McHaffie and N. D. Clare, *J. Ind. Eng. Chem.*, 17, 381, 1925.

acid end, where the area attacked was small, and an appreciable effect at the less acid end of the  $p_{\rm H}$  range where it is large.

The marked contrast in the appearance of specimens corroded aboveand below  $p_{\rm H}$  4, when air was present, is of particular interest, since it provides visible evidence for the transition at  $p_{\rm H}$  4·3, noted by Speller and others, between the hydrogen evolution and the oxidation types of corrosion. The fact that the presence of oxygen, even in small traces, induced this transition suggests that the protection of certain areas, at low acidity, was due to the formation of a film of oxide, an explanation which is in accordance with the work of others. Possibly the concentration-cell effects observed by McKay 10 may also be of importance in bringing about this distribution of corrosion. It may be suggested that at high acidity, the attack develops preferentially at the edges, because suitable nuclei for the formation of bubbles of hydrogen are more likely to be found at these regions than elsewhere; moreover, the hydrogen ion concentration is better miantained and the products of corrosion are more readily removed at regions near the edges than. at other parts of the surface of the metal.

The statement of Speller 11 with regard to the effect of oxygen on corrosion is well illustrated in Fig. 1, which shows that oxygen greatly increased the corrosion in the less acid members of the series and that its influence declined rapidly with increasing acidity. Depolarisation of hydrogen, however, is not unimportant at high acidity, since it has been shown (p. 1200) that there was no great variation in the amount of hydrogen depolarised over the whole  $p_{\rm H}$  range. The fact that the total corrosion at high acidity (pH 2.4) was much the same in the presence and absence of oxygen can be explained on the grounds that the corrosion by oxidation was balanced by an almost equivalent inhibition of the hydrogen-evolution type of corrosion.

The curves of Fig. 4 and the data in Table I. reveal the remarkable fact, not fully understood that corrosion and the evolution of hydrogen were both greater initially, at low, than at high acidity, although they were ultimately much the greatest at pH 2.4. The work of Van Name and Bosworth 12 suggests that the stirring caused by the evolution of hydrogen, actually induced more rapid corrosion of the metal, and since bubbles were only visible below  $p_{\rm H}$  4, this may account for the increasing steepness of the curves with time.

This view is supported by the evidence given by curves AI and BI of Fig. 5 and the figures of Table III. (C), which suggests that ferric iron, in acting as a depolariser at high acidity, reduces the evolution of hydrogen with its consequent stirring effect and that this results in decreased corrosion.

The divergence between curves BI (citric acid + ferric iron) and A2 (citric acid + oxygen) of Fig. 5, at the more acid end of the  $p_{\rm H}$ -range, may be attributed to the greater concentration of ferric iron, at high acidity, in Experiment III. than in Experiment II., previous work 13: having proved that the rate of oxidation of ferrous to ferric iron by air is relatively slow at this acidity. In comparing these two curves with the basal curve AI of Fig. 5 we see that, while ferric iron stimulated

<sup>&</sup>lt;sup>9</sup> F. N. Speller, Corrosion—Causes and Prevention, p. 26, Table V., 1928. <sup>10</sup> R. J. McKay, Trans. Am. Electrochem. Soc., 41, 201, 1922.

F. N. Speller, Corrosion—Causes and Prevention, p. 29, 1928.
 R. G. Van Name and R. S. Bosworth, Am. Journ. Sci., 32, 217, 1911.

<sup>13</sup> Trans. Faraday Soc., 29, 832, 1933.

corrosion at low acidity, free oxygen promoted it to a still greater extent. Table III. shows that the increase of corrosion by ferric iron was through its action as a depolariser of hydrogen; free oxygen, on the other hand, acted not only as a depolariser but actually stimulated the evolution of hydrogen (see Fig. 3). The cause of this stimulation is not clear, but Table I. shows that it is mainly an initial effect and it may be suggested that the evolution of hydrogen is inhibited by dissolved iron, since the action of iron as an oxygen-carrier (see p. 1207) becomes of increasing importance as corrosion proceeds and less free oxygen reaches the surface of the metal.

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## THE FORMATION OF OXIDE FILMS ON GOLD AND IRON.

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In a previous paper 1 it was shown that in the case of a gold anode passivated in acid chloride solutions the recovery of the active state could be regarded as coinciding with the solution of a film of gold peroxide. The gold peroxide present on a fully passive electrode first of all reacted with the chloride ion of the solution leaving a film of lower gold oxide. If the solution contained no free acid, and was agitated slightly to prevent local accumulations of acid (products of hydrolysis of chlorine), around the electrode, then the film of lower oxide remained on the surface of the gold. The subsequent application of a current too small to cause passivation under ordinary circumstances led to the practically instantaneous attainment of the passive potential and evolution of chlorine.

It has been shown that oxide films are frequently present on the surface of metals which have become resistant to atmospheric corrosion,<sup>2</sup> and even in the case of copper, Vernon<sup>3</sup> detected the formation of a thin invisible oxide film by heat treatment of the metal. This film protects the copper from oxidation by air in a remarkable manner. In view of this fact it was of interest to attempt to determine whether the freedom from corrosion of such a noble metal as gold should be ascribed to the presence of an oxide film, or if the cause lies rather in some intrinsic property of the metal which manifests itself as the characteristic highly positive electrode potential with respect to hydrogen. On a classical basis such a potential would imply but a small affinity for oxygen.

To test whether the general results obtained with gold would also apply to some other metals which exhibit the phenomenon of ready passivation under suitable anodic conditions, some measurements were also made on iron.

<sup>1</sup> Shutt and Walton, Trans. Faraday Soc., 28, 740, 1932.

<sup>&</sup>lt;sup>2</sup> Hedges, Protective Films on Metals, Chap. III. (Chapman and Hall).

<sup>&</sup>lt;sup>3</sup> Vernon, J.C.S., 1926, 2273.

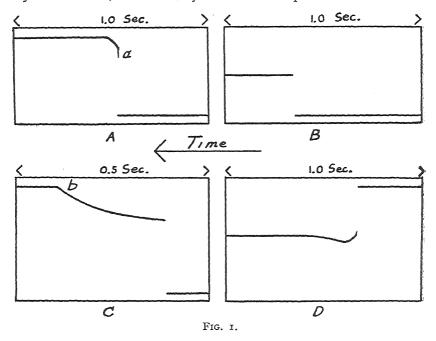
### Experimental.

For potential-time measurements the apparatus used was the high frequency, high resistance voltmeter system previously described, and the gold electrodes were similar to those employed in the previous work. Two samples of iron were examined: one a specimen of commercial Swedish iron and the other some electrolytic sheet prepared in the laboratory and annealed at high temperature in a vacuum furnace in such a way that freedom from adsorbed hydrogen was as far as possible assured. Under these conditions the actual crystals of the electrodeposited metal were so large as to be easily visible to the eye. No difference could be detected between the behaviour of the two samples of iron in the experiments described.

### Results and Discussion.

### A. Gold.

From the previous work it was clear that if gold be treated with hydrochloric acid, solution of any oxide film takes place and the electrode



becomes fully active. On making such an "active" electrode the anode in a cell containing a vigorously stirred solution of potassium chloride, quantitative solution of the metal took place up to a certain limiting current density. This limit occurred at 0.60 amps. per cm.² in normal potassium chloride solution at 25° C. At this or higher current densities, the electrode dissolved at first but eventually passivated.

The behaviour of a gold plate carrying an oxide film—produced, for example, by anodic passivation in a separate cell—was, however, entirely different. The nature of this difference is perhaps best indicated by reference to the oscillograms reproduced in Fig. 1. In these diagrams increases of the electrode potential are shown by a vertical displacement upwards of the oscillograph tracing. Diagram A of this figure shows.

the potential change which occurred when a current density of o.30 amps. per cm.<sup>2</sup> was applied to an electrode covered with the oxide film. The voltage rose immediately to a value represented by the point a, which is nearly equal to that required for chlorine evolution, and a short time sufficed for development of the full chlorine potential (about 2·I volts, when allowance is made for the excess potential due to the ohmic drop across the solution between the electrode and the tip of the standard calomel half element). B shows the behaviour of a similar electrode activated by dilute hydrochloric acid prior to immersion in the potassium chloride, the same "test" current of 0.3 amps. per cm.2 being employed. The steady potential recorded under these circumstances was the 1.3-1.4 volts characteristic of gold solution. The complete absence of gas bubbles and continuation of the relatively low potential showed that this process would proceed indefinitely. Curve C is included to indicate the break which occurred when the current density applied to the same electrode as in B was raised above 0.6 amps. per cm.<sup>2</sup>. The potential at first was about 1.3 volts, indicating smooth solution of gold, but with continued electrolysis the voltage rose, slowly at first but finally rapildy until at b a potential of 2·I-2·2 volts was reached, when bubbles of chlorine could be seen to rise from the electrode. Even at much higher current densities the break in the potential curve corresponding to the initial solution of gold, could always be seen in the case of an electrode fully active; the curve was never of the type shown at A.

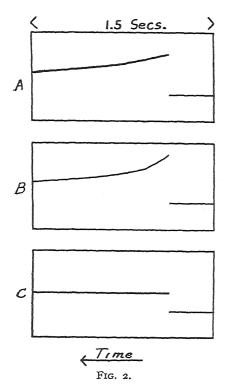
These points of difference between the potential variations observed at the electrode on application of the test current formed for subsequent work the means of distinction between gold plates covered with oxide film and those with a clean active surface. Using this experimental method it was soon found that anodic passivation was not the sole means of production of the oxide film. Prolonged exposure to the atmosphere, treatment with an alkaline hypochlorite or hypobromite solution and even alkali alone all resulted in film formation. Other oxidising agents such as nitric acid, permanganate and hydrogen peroxide were tested but no film could be detected on the surface of the metal as a result of their action.

The behaviour of a gold anode in potassium chloride solutions containing small quantities of alkali is noteworthy. As would be expected, a passive gold anode does not recover its active state in such a solution. After cathodic reduction, however, the electrode could be obtained active and would dissolve up to an appreciable current density. Thus in a solution of normal KCl, 0.0024 N with respect to KOH, ( $p_{\rm H} = 10.8$ ) gold would dissolve up to a current density of 0.40 amps./cm.2. If, however, the current was switched off from such an electrode dissolving actively, then the potential subsequently exhibited a minimum as shown in Fig. 1, D. This change is similar to that observed by Smits 4 in the case of iron and nickel dissolving in solutions of their chlorides, although the explanation offered was entirely different from that here suggested. On the reapplication of the current to the electrode, gas was immediately evolved indicating the presence of a film of gold oxide, just as would have been produced had the electrode been anodically passivated in potassium chloride solution. Further experiments showed that if a gold electrode, previously treated with hydrochloric acid to ensure freedom from oxide, were immersed in the above solution then the potential passed through a minimum as Subsequent test with a current showed again the presence of an oxide film on the electrode. Thus it seems clear that the film is formed by chemical action of the alkali on the metal. This reaction is apparently retarded sufficiently by previous cathodic reduction to enable the electrode to be anodically dissolved. On this basis the rise in potential in Fig. 1 D could be explained by the oxidation of the hydrogen which is shown below to be of necessity produced in the formation of the film.

Smits, A Theory of Allotropy (Longman), p. 367.

In chloride solutions containing alkali stronger than 0 0025 N it was impossible to obtain solution of the metal, a few milliamps. being sufficient to cause evolution of gas, even after the metal had been reduced by temporary reversal of the current.

The oscillograms A and B of Fig. 2 show the results of the application of test currents of values 9 and 22 M.A./cm.² respectively to a gold electrode placed in a normal KCl solution after treatment with 0.5 N KOH. Fig. 2 C is introduced for comparison and shows the behaviour of an active gold electrode at 9 M.A./cm.² in the same chloride solution. It will be seen that in both A and B the electrode potential at first rises above the value at which gold dissolves, but subsequently falls to that value. The gold finally dissolves in the same way as does a fully active electrode, and eventually the current can be increased to the same value as is possible



on fully active gold. At values of the current density much above 22 M.A./cm.2 the electrode was instantly passive as in Fig. 1 A. From these results it is apparent that under certain circumstances, after treatment with alkali, the electrode is covered by a film of gold oxide which is porous and incomplete. At very low current densities the gold dissolves in the pores, resulting finally in the dislodgement of the film. higher current densities the instant passivation is considered to indicate that the oxide film is immediately oxidised to peroxide and the film is completed. From further experiments of the same type it became evident that the degree of porosity of the film depended on the previous treatment of the electrode. The more intense the alkali treatment (in terms of time of immersion and concentration of KOH), the lower the current density at which the electrode was instantly passiv-A complete film, however, was readily obtained by immersion in alkaline chlorine solution. After this treatment a current density of 2 M.A./cm.2 was sufficient to cause chlorine evolution.

In the previous work  $^1$  it was shown that the magnitude of the passivation film in hydrochloric acid solutions corresponded to between  $_2\cdot 6$  and  $_3\cdot 6$  molecular layers of  $\mathrm{Au_2O_4}$ . This measurement was of necessity made on a surface considerably etched. The weight of such a film would be very small and detectable by direct weighing only with difficulty. The observation, however, that treatment with certain solutions resulted in the rapid formation of a film indicated that the alternate immersion in such a solution and dilute hydrochloric acid might, on continued repetition, result in an easily measurable loss of weight.

By assuming a simple cubic arrangement of atoms in the metal surface it can be shown that the weight of one atomic layer on a gold surface I square centimetre in area is about  $5 \times 10^{-7}$  gm. Thus in one hundred immersions the loss in weight which might be expected, assuming the

oxidation of one atomic layer for each individual film formed, would be about 0.00005 gm. per cm.2 of electrode surface. Experiment showed that the time necessary for formation of the film was very small (of the order of 1 or 2 seconds) and a similar time sufficed for its removal in 0.5 NHCl. An apparatus was therefore constructed which would immerse a piece of gold successively in four dishes containing solutions of KOH, water, HCl and water respectively. The time of immersion was initially approximately 12 seconds in each solution. After a large number of immersions in the above solutions, a gold electrode showed no detectable loss of weight. The reason for this was readily shown by a further experiment. It was observed that an electrode was regularly passivated by the KOH for the first few revolutions of the apparatus but beyond this gold was found to be entirely impervious to attack by KOH and remained persistently active on test in KCl solutions. Furthermore an electrode allowed to stand in KOH for about 30 minutes and subsequently treated with hydrochloric acid showed no formation of oxide film after being returned to the KOH solution. After being dissolved anodically, however, in KCl solution for a short time, the electrode was again readily passivated by the alkali. It is considered improbable that the oxide film formed by alkali is due to traces of oxygen or chlorine remaining in the electrode from previous anodic treatment since any such oxide should be removed by merely treating the electrode with acid, and subsequent immersion in alkali would then have no effect.

In view of the strong indications that alkaline hypochlorite induces the formation of a complete, non-porous film on gold it was decided to investigate quantitatively the effect of repeated immersions of an electrode in hypochlorite and in hydrochloric acid solutions, with intermediate rinsing with water. It was at once apparent that considerable solution of gold was taking place. In early experiments the loss in weight per cycle of immersions was found to represent a large number of atomic layers of gold (about 30). On increasing the time of immersion however, and arranging that a jet of water should impinge directly on the electrode before each treatment with the hypochlorite or acid, the loss in weight corresponded, within experimental error, to the removal of one layer of gold atoms for each revolution of the apparatus. For two fresh pieces of gold sheet, dipped in identical solutions of acid and hypochlorite, the weight losses per cm.² per revolution were found to be  $4.58 \times 10^{-7}$  and  $5.6 \times 10^{-7}$  gm. whilst the loss to be expected on the basis of a unimolecular film of the type  $\text{AuO}_x$  is about  $5 \times 10^{-7}$  gm. The effect of concentration of hypochlorite was tested, with the following results:—

NaOCl.			Loss in weight/revolution.
0·16 N	•		. $4.9 \times 10^{-7}$ gm.
0·16 N		•	. 5·6 × 10− <sup>7</sup> ,,
1·6 N		•	$.6.2 \times 10^{-7}$ ,,
1·6 N			$.6.3 \times 10^{-7}$ ,,

It is considered that, within the experimental error, the weight loss was constant, in spite of the ten-fold variation in concentration of available chlorine. Other experimental conditions—strength of hydrochloric acid, efficiency of washing—were maintained constant throughout the series. It is considered that the experimental conditions and results preclude any suggestion of direct attack of the gold by chlorine liberated in the acid bath from hypochlorite carried over by an incompletely washed electrode. It is suggested that the mechanism of solution comprises the oxidation of the metal by the alkaline hypochlorite with subsequent solution of the oxide film (one molecule in thickness) in hydrochloric acid.

The foregoing observations are not easily explained on the basis of the classical theories of electrode action; especially difficult is the unexpected behaviour of a gold electrode which has had prolonged treatment with alkali and subsequent removal of its oxide film by acid. The strongly marked negative potential of such an electrode and the refusal to passivate on reimmersion in alkali are remarkable.

The following is suggested as a theory which accords with the experimental observations. A gold electrode, on being immersed in alkali solution is considered to acquire a film of Au<sub>2</sub>O<sub>3</sub>, the film being approximately monomolecular in thickness, since it is sufficient to protect the electrode against anodic solution, and result in full passivation. It may, under certain conditions, be slightly porous since gold will dissolve at low current densities after immersion in KOH for a short time. This conclusion being granted and discounting the likelihood of atmospheric oxidation, it is difficult to avoid the assumption that hydrogen must be evolved simultaneously by some such mechanism as

$$Au + 3H2O \rightarrow Au(OH)3 + 3H$$
  

$$Au + 3OH' + 3H \rightarrow Au(OH)3 + 3H.$$

or

The quantity of hydrogen liberated by formation of such a small quantity of oxide is minute and should, if liberated as gas, pass into solution. The relative positions of gold and hydrogen in the electromotive series, however, render extremely unlikely the formation of even the most minute quantity of gaseous hydrogen (under the experimental conditions). The hydrogen may, however, be adsorbed along with the oxygen (or hydroxyl groups), and with its relatively greater mobility may penetrate to the underlying atoms while the surface of the metal is fully oxidised. When such a "loaded" electrode is treated with acid, the surface film is dissolved away and the gold atoms carrying adsorbed hydrogen are exposed. Assuming that atoms of gold carrying hydrogen are no longer capable of adsorbing oxygen, the mechanism by which further passivation is prevented becomes evident. In this connection the work of Bengough, Lee and Wormwell 5 might be quoted. They suggest that when zinc is placed in salt solution, hydrogen is liberated at a multiplicity of points, and corrosion proceeds at a rate directly proportional to the oxygen supplied, the latter acting as a depolariser for the hydrogen. If this representation is true, it is evident that the hydrogen on gold is only removed with difficulty, since, of all the oxidising agents tested chlorine (or hypochlorite) alone is capable of oxidising the hydrogen rapidly and restoring the electrode to the state in which it is capable of passivation by KOH. Other oxidising solutions such as hypobromite, conc. HNO<sub>3</sub> or acid permanganate, remove the adsorbed hydrogen relatively slowly. Hydrogen peroxide did not appear to affect the hydrogen even during a period of several hours. It is likely that this adsorbed hydrogen is to some extent electromotively active, as gold which has stood in KOH always assumes, on immersion in HCl, a potential negative by a considerable amount to an ordinary "active" electrode. This behaviour suggested that the potential might show itself to be a function of the  $p_{\mathbb{H}}$  of the solution.

With a view to testing the reversibility of the adsorbed hydrogen, some observations of the potential of a gold electrode, with and without adsorbed hydrogen, have been made in solutions of varying  $p_{\rm H}$ . For this purpose the apparatus used was a high resistance null point valve potentiometer system, of the type employed for  $p_{\rm H}$  measurements with a glass electrode. This method allowed the potential of an electrode

Bengough, Lee, and Wormwell, Proc. Roy. Soc., 131A, 494, 1931.
 Harrison, J.C.S., 1930, 1528.

to be measured without introducing any errors due to polarisation by the

measuring system.

After standing in alkali, so that some adsorbed hydrogen was present, the potential of an electrode in 2 N hydrochloric acid was 0.42 volts positive to N hydrogen, whilst after treatment with alkaline hypochlorite, to remove any adsorbed hydrogen, the potential was + 0.954 volts. The subsequent changes in potential, on standing in 2 N hydrochloric acid, depended entirely on the time of pre-immersion in alkali. If this time were short, then the potential rose to a value of 0.73 volts after a few hours. After prolonged immersion, however, the potential was only 0.40 volts, and remained at about that value for at least three days. On neutralisation of the acid with KOH solution the potential of the hydrogenated electrode, originally at about 0.73 volts, fell considerably, until at the point of neutralisation the potential was 0.54 volts, and on addition of alkali fell rapidly to an even lower value. In contrast to this behaviour, an electrode, which had been standing in NaOCl solution, fell rapidly from 0.95 to 0.73 volts, but only changed slowly on neutralisation to 0.69 volts. With further addition of alkali, the potential fell more slowly than did that of the previous electrode, but finally reached the same potential in strong KOH solution of o 10 volts positive to normal hydrogen. Thus a gold electrode which has been treated with KOH solution does behave qualitatively as a hydrogen electrode and might, in conjunction with the electrometer valve system, be used for electrometric titrations, although the actual potentials are far removed from those of a hydrogen electrode in equilibrium with one atmosphere of the gas. On the other hand an electrode from which any adsorbed hydrogen had been removed showed little change in potential with variation in  $p_{\rm H}$  so long as the formation of adsorbed hydrogen was prevented by maintaining the solution acid.

### B. Iron.

It was of interest to determine whether the behaviour of such a base metal as iron is qualitatively similar to that of gold. It has been shown by W. J. Müller 7 that a fresh iron electrode placed in a neutral solution of sodium sulphate exhibits an extraordinarily short time of passivation, but that after continued reduction and treatment with acid, the metal requires the same passivation time as in acid solution. This is attributed to the presence of an oxide film formed in air, such as has been shown to exist by U. R. Evans.<sup>8</sup>

Experiment indicated that, as in the case of gold in KCl solution, a passivated iron electrode retained in a solution of potassium sulphate, a film of iron oxide, which led to a potential-time curve of the type in Fig. 1 A at a low current density. As before, if the solution were unstirred, then the electrode recovered its active state through the action of the acid anolyte. It was further observed that if an electrode were allowed to stand in neutral  $K_2 SO_4$  solution then the potential became more negative at first, but subsequently rose again in exactly the same manner as did a gold electrode in an alkaline solution of KCl. Application of a test current subsequently showed the presence of an oxide film on the surface of the metal. The rise in potential was produced much more rapidly when the electrolyte was stirred, apparently owing to the greater rate at which hydrogen could be removed through oxidation by dissolved oxygen. In the case of iron the formation of the film in neutral solution might occupy several minutes, and under

<sup>&</sup>lt;sup>7</sup> W. J. Müller, Trans. Faraday Soc., **27**, 737, 1931. <sup>8</sup> Evans, J.C.S., 1021, 1927.

these circumtances the presence of a partial film was shown merely in a reduction of the current necessary to cause passivation.

Treatment with alkali, or even distilled water accelerated the formation of the film. Cathodic reduction, with its consequent saturation of the electrode with hydrogen, greatly retarded the spontaneous passivation of the electrode.

The formation of adsorbed hydrogen under such conditions has been previously suggested by Andrew 9 who found that the properties of iron were considerably modified by prolonged treatment with alkalies.

### Conclusion and Summary.

It has been shown that gold is rendered passive by treatment with alkalies; on the basis of the oxide film theory of passivity this is explained by the interaction of gold with the solution to form a layer of gold oxide, which on subsequent anodic treatment renders the electrode fully passive. Accompanying the formation of the oxide, hydrogen is liberated and adsorbed on the gold. The oxide film is readily dissolved in dilute hydrochloric acid, but the hydrogen remains adsorbed and when present in sufficient quantity prevents the further action of alkalies. Under conditions which allow of removal of hydrogen by oxidation, such as the presence of alkaline hypochlorite, the loss in weight of a gold surface on subsequent treatment with acid has been shown to correspond closely to that expected by the formation of a monomolecular layer of gold oxide at each immersion in the oxidising solution.

In solutions of low OH' concentration containing oxidising agents, such as concentrated nitric acid or acid permanganate, the formation of a film was not detected. This might be due to the slow action of these solutions in removing the adsorbed hydrogen and to the low hydroxyl ion concentration with the subsequent slowness of the reaction to give the gold oxide.

The presence of adsorbed hydrogen on the metal manifests itself in the more negative potential exhibited by an electrode so charged. The potential of an electrode containing adsorbed hydrogen in acid solutions, falls more rapidly, with an increase of  $p_{\rm H}$ , than does that of one from which the adsorbed hydrogen has been removed by treatment with chlorine. In alkaline solution, where more adsorbed hydrogen is readily produced, the potential of both electrodes is the same.

The behaviour of iron is qualitatively similar to that of gold. A film of oxide is readily formed by treatment with either neutral or alkaline solutions. The formation of the film was accompanied by a lowering of the potential of the electrode, but on standing, this rose again to the former value. In this case the dissolved oxygen is sufficient to cause oxidation of the adsorbed hydrogen.

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9 Andrew, Trans. Faraday Soc., 9, 316, 1913-14.

## STUDIES IN GELS IV.—THE SWELLING OF SILICA GEL.

By D. G. R. BONNELL.

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It has been found desirable, for practical reasons, to classify gels into two general groups (a) elastic or swelling, and (b) non-elastic or non-swelling gels. The members of the first group, when suspended in certain liquids, possess the property of imbibing some of the liquid and swelling; for example, when a sample of gelatine gel is placed in water it absorbs some of the liquid and increases in volume. On the other hand, gels included in the second group do not swell when placed in a liquid medium, although they may absorb some of the liquid. Silica gel is usually taken as being a typical example of the second group. When a sample of silica gel of low water content is placed in water the volume changes which take place by absorption of water are insignificant.

During the course of investigations on the properties of silica gels, it was observed that under certain conditions the fresh gel could imbibe a large volume of water, and the following is a short account of a few simple experiments which were carried out in order to find out the conditions under which this imbibition of water could take place.

### Experimental.

During the storage of some specimens of silica gel of geometrical shape in distilled water at temperatures near the boiling-point, it was observed that the samples lost their angular contours, i.e., the sharply defined edges gradually disappeared, being replaced by smooth rounded countours, the gels simultaneously becoming less opalescent and more transparent. As a result of this observation the process was investigated more carefully, and for this purpose small cones of gel (about 15 grams in weight) were prepared from sodium silicate and hydrochloric acid as described in Part I.¹ of this series. These cones were allowed to synerise for about ten days and then immersed in distilled water kept at 70° C. During the first three days, the water was changed every 24 hours. At the end of this period it was found that the electrolyte concentration of the fresh water, after 24 hours contact with the gel, was negligible, and, consequently it was decided that further changing of the water was unnecessary until the gel samples were removed for examination.

No visible changes in the appearance of the gel were observed until the fourth day. At the end of this time marked signs of softening were visible—the sharp edges of the cone being much less well-defined. By the end of the sixth day the gel had practically lost its opalescence and become nearly transparent. The gel sample was definitely softer than the comparatively hard gel obtained at the end of the syneresis period; indeed to the touch it resembled a weak jelly. This softening process progressed as time elapsed until at the end of the eighth day the gel was so soft that it gave way under the lightest touch. In fact, when the water was siphoned away, the gel simply collapsed into a comparatively thin layer of gel

on the bottom of the containing vessel. In its behaviour, it was identical with that of a very dilute gel, which is too weak to support its own weight.

This points to the dilution of the gel by the imbibition of more water and in order to test whether this was the case, analyses were made on a sample of gel before and during treatment. A typical example of the results obtained is as follows:—

```
Water content of gel as prepared = 90 per cent.

Water content of gel after syneresis = 86 ,,

Water content of gel after 5 days treatment = 94.5 ,,

Water content of gel after 10 days treatment = 96 ,,
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It should be pointed out that in order to increase the water content from 86 per cent. to 96 per cent., 100 grams of the gel must absorb roughly about 250 grams of water. The above values therefore show that the gel has actually sorbed a large quantity of water during treatment, the water content at the end of five days having attained a value far above that of the original gel before syneresis. This means that the concentration process which took place during syneresis had been reversed.

It was observed that the liquid in which the gel samples were stored during the treatment became more and more opalescent with increasing time of exposure. At the end of about six days the liquid showed strong opalescence and gave, with a beam of light, a strong Tyndall cone indicating the formation of a silica sol. In order to determine the variation of the silica concentration of the storage liquid with time, analyses were carried out during the whole time of exposure of a gel sample—after the removal of all the electrolyte present. These showed that the silica concentration steadily increased until a value of  $o \cdot 5$  per cent.  $SiO_2$  was attained, after which no further increase was obtained. When at this stage the liquid was replaced with distilled water, the same increase in SiO<sub>2</sub> content was obtained up to the same limiting value. By repeatedly changing the storage liquid in this way, the whole of the gel could be completely dispersed into the sol state. It was found impossible to increase the silica concentration of the liquid in contact with the gel even by heating on a water bath for several days-the volume of the liquid was, of course, kept constant throughout. This seems to indicate that the complete dispersion of the gel will not take place in a liquid of higher silica content than 0.5 per cent. SiO2.

The sol thus formed is quite stable, no trace of coagulation being ob-

### TABLE I.

Water content of—
gel after syneresis = 86 o per cent.
swollen gel = 95 o ,, ,,
gel at end of 478 hours = 88 o ,, ,,

., ., .,
Liquid in Grams. Exuded per 100 Grams G
10-4
13.0
14•5
19.6
26.2
31.8
37.7
39.2
40.8
51.0
53.6

servable at the end of several months. Filtration through a "9" membranfilter"—as supplied by the Membranfilter Gesellschaft Göttingen—showed that 95 per cent. of the total silica was retained on the filter. Since the average size of the pores of such a filter is of the order of 60-70 μμ the silica is present in the sol as fairly coarse particles.

This swelling effect of high temperature treatment suggested that the contraction process causing exudation of liquid during syneresis had been reversed. A study of the behaviour of the swollen gel when placed in the synerometer

and kept at 20° C. showed that under these circumstances it exuded liquid in a similar manner as in syneresis. A typical example of the results obtained is reproduced in Table I.

The data show that the liquid is not exuded very rapidly and the equilibrium value is only attained after a considerable period. When the volume of liquid is plotted against time, a smooth curve is obtained of identical form to those obtained for syneresis—the velocity of exudation being high initially but slowly decreasing with time.

If at the end of this exudation period a sample of the contracted gel was replaced in the hot bath, it reabsorbed more liquid, ultimately again reaching the dilute and swollen state. The following data show the vari-

ation of the water content of a gel sample with the time of exposure before and after being kept in the synerometer.

These values show that the cycle can probably be repeated indefinitely.

In no case was it found that all the imbibed liquid was exuded in the synerometer although, as Table I.

TABLE II.

		Water Content.			
Treatment.			Sample A. Per Cent.	Sample B. Per Cent.	
Immediately after sy	nere	esis.	86.2	_	
5 days in hot bath		.	94.3		
7 days in hot bath		.	95.6	-	
12 days in hot bath		. [	97.0		
After exudation.		.	93	89.6	
5 days in hot bath	•	.	96•3	93.6	
15 days in hot bath	•	•		95.3	

shows, the experiment was continued in some cases for about three weeks. Even at the end of this time the gel had not reached equilibrium but was still exuding appreciable quantities of liquid. Furthermore, examination of the gel at the end of the experiment showed that it was still quite soft and more jelly like than the comparatively hard gel after syneresis. This was also true of treated samples kept in equilibrium with their own vapour for over eighteen months. Water content analysis led to the same conclusion. These effects indicate that the exudation of liquid is probably due to different forces from those causing the spontaneous contraction during syneresis.

It is well known that syneresis takes place even when the gel is stored under water, and for further comparison the following experiment was carried out. A sample of gel was first submitted to heat treatment until the water content reached the value of 95 per cent. and then placed in a bath of distilled water at 20° C. Analyses at the end of seven days and sixteen days storage showed no decrease in the water content, proving that no exudation of liquid took place under these circumstances. From this result it can be concluded that the exudation of liquid from the swollen gel in the synerometer is not due to the same cause as that of the irreversible syneresis which takes place under water or to the temperature drop from 70° C. to 20° C.

On the other hand when the gel is in such a dilute state, its density differs very little from that of distilled water, so that when placed in such a medium it does not support any appreciable hydrostatic pressure due to its own weight. This is, however, not true when the gel is in the synerometer, as in this case it is compelled to support its weight throughout the experiment. It seems very probable therefore that the whole effect in the latter case may be due to the hydrostatic pressure on the dilute gel

On the strength of the above results further tests were carried out in order to determine the behaviour of the gel when stored in electrolyte solutions.

Gel samples stored for long periods in their own syneretic liquid showed no tendency to swell, the water content remaining constant throughout the treatment. The same result was obtained with storage in 1 per cent.

and o'r per cent. sodium chloride solutions, while with o'or per cent. sodium chloride solution imbibition took place but more slowly than with the highly dialysed gel. From this it may be concluded that for a large water absorption the electrolyte must be reduced to very low concentrations.

This imbibition could also be inhibited by reducing the water content of the gel specimen. Gels whose water content was below 75 per cent. showed the effect only to a small extent. As the water content increased so did the rate of absorption of water increase, e.g., a gel of 75 per cent. water only increased to 87 per cent. after six weeks while a gel of 84 5 per

cent. water increased to 95.5 per cent. in four days.

This inhibiting effect of reducing the water content seems to imply that the mobility of the silica micelles is an important factor in the process of swelling, although a number of other factors such as the osmotic forces set up inside the gel structure through the presence of electrolyte, the coagulating effect of the electrolyte, the decreased viscosity of the water at these temperatures may also be operative.

### Conclusions.

From the above simple experiments it is clear that under certain circumstances the imbibition and exudation of water by silica gel can be a reversible process. Under the conditions described electrolytefree silica gel behaves in a similar manner to a typical elastic gel, viz., when placed in warm water it imbibes a large quantity of water, swells and is gradually peptised into the sol state. One very important difference lies in the high sensitiveness of the silica gel to the presence of electrolyte.

The fact that the gel readily exudes a large proportion of the imbibed liquid when exposed to a low hydrostatic pressure, e.g., its own weight, shows that the swelling pressure at these dilutions is comparatively

small.

### Summary.

The effect of storing fresh silica gel in electrolyte free water at a temperature of about 70° C. has been investigated.

It has been found that under certain circumstances silica gel will imbibe

large quantities of water similar to a typical elastic gel.

The author wishes to express his thanks to the Director of Building Research for kind permission to publish these results.

Building Research Station, Bucknall's Lane, Garston, Herts.

## STUDIES IN GELS V.—EFFECT OF NEUTRAL ELECTROLYTES ON THE SYNERESIS OF SILICA GELS.

By D. G. R. BONNELL.

### Received 3rd August, 1933.

Examination of the literature shows that although several workers have investigated the effect of free acids and alkalies on the syneresis of various gels, 1 yet very little work has been done on the effect of the presence of neutral salts on the phenomenon of syneresis.

Prakash and Dhar <sup>2</sup> have studied the influence of the concentration of the coagulating electrolytes on the syneresis of numerous inorganic jellies, e.g., ferric phosphate and arsenate, hydroxides of vanadium and zirconium, etc. They found that in all cases the amount of liquid exuded at the end of either 90 minutes or 24 hours increased with increasing concentration of electrolyte. The progress of syneresis with time was, however, not followed. These authors have also investigated the influence of electrolytes on the syneresis and clotting of blood <sup>3</sup> and come to the conclusion that as the concentration of electrolyte increases the amount of syneresis gradually decreases.

As far as can be ascertained no work has been done on the effect of the concentration of neutral electrolytes on the syneresis of silica gels and this investigation was carried out in an endeavour to obtain information on this subject.

### Experimental.

Previous investigations <sup>1</sup> have shown that, in order to estimate the effect of the electrolyte content, it is essential to maintain the silica concentration and the hydrogen ion concentration of the silica sols constant throughout the series of experiments and for this purpose the following procedure was adopted.

To obtain the initial sol a measured volume of about 6 N acid was diluted with a known volume of distilled water and then mixed with a known quantity of sodium silicate solution. For the preparation of a series of sols differing only in electrolyte content, different measured amounts of the distilled water were replaced by the same volumes of a saturated solution of the particular salt to be investigated, in so doing care being taken to maintain the total volume of the sol constant. In this way the silica concentration was kept constant as the small changes due to the greater density of the salt solution may be neglected.

Since the  $p_{\rm H}$  values of the salt solutions were in the neighbourhood of 6·5, it was decided to work with gels of this  $p_{\rm H}$  value, so that the addition of varying amounts of the salt solutions had practically no effect on the ultimate  $p_{\rm H}$  of the sol. Even assuming small variations to occur, they would not appreciably affect the results, as, in this region, syneresis is not very sensitive to slight changes in hydrogen ion concentration (cf., Part II. of this series).

<sup>&</sup>lt;sup>1</sup> Compare parts I. and II. of this series. Trans. Faraday Soc., 28, 1, 11, 1932.

Prakash and Dhar. J. Ind. Chem. Soc., 7, 417, 1930.
 Prakash and Dhar, J. Physic. Chem., 35, 629, 1931.

### 1222 ELECTROLYTES AND THE SYNERESIS OF SILICA GELS

The progress of syneresis was followed by the method described in Part I. of these investigations, while the salts used were pure analytical reagents. The temperature was kept constant at 20° C. throughout the investigation.

### Results.\*

(a) Gels prepared with hydrochloric acid. Silica concentration = 8.4 per cent. SiO<sub>2</sub>. Original NaCl concentration = 5.04 per cent.

TABLE I.

Added Salt Concentration Per Cent.	Setting Time in Secs.	Induction Period in Secs.	Time in Hrs. after Setting.	Wt. of Liquid in Grams Synerised Per 100 Grams Gel.
Electrolyte NaCl:				
0.0	30	50	2·0 4·5 22·0	8·430 10·800 14·858
			98.5	16.660
1.44	18	36	1.0	7.542
			4·5 24·5 187·5	13·373 17·668 20·401
2-88	15	25	2.0	10.244
			3·0 23·0 123·5	12·524 16·690 18·713
4*32	13	18	1.0 3.0 22.0 74.0	5·504 10·369 15·510 17·180
Electrolyte KCl:			,,,	1,100
1.355	19	36	1·5 5·0 23·6 124·0	8·607 13·536 19·151 22·593
2.71	15	30	1·0 5·0 214·5	9·241 14·078 19·661
4*065	12	22	1·5 10·0 22·0 210·5	7:535 11:437 13:344 15:908
Electrolyte Na <sub>2</sub> SO <sub>4</sub> :				13 900
0.173	23	33	2·0 6·0 19·0	12·170 15·484 17·783
			139.0	20.392
•356	16	26	2·0 5·0 22·5 167·5	12·619 14·431 17·470 19·694
•519	12	15 .	2.0 5.0 22.0 118.0	10·999 14·002 16·499 18·253

<sup>\*</sup> For each electrolyte concentration only the early and final values are given in tables I. and II.

TABLE I.—continued.

Added Salt Concentration Per Cent.	Setting Time in Secs.	Induction Period in Secs.	Time in Hrs. after Setting.	Wt. of Liquid in Grams Synerised Per 100 Grams Gel.
Electrolyte K2SO4:				41
0.246	20	30	2.0	9.968
	]		6•0	14.065
•			22.0	16.857
	1.		167.0	19.715
•492	10	20	1.2	10.386
			4.2	13.126
			23.0	16.002
			165.0	17.930
•738	8	17	. 3·o	ro-947
,			20.75	15.481
			67.0	16.589
<b>.</b>			163.0	17.764

<sup>(</sup>b) Gels prepared with sulphuric acid. Silica concentration = 8.05 per cent. Original Na<sub>2</sub>SO<sub>4</sub> concentration = 3.7 per cent.

TABLE II.

Added Salt Concentration Per Cent.	Setting Time in Secs.	Induction Period in Secs.	Time in Hrs. After Setting.	Wt. of Liquid in Grams Synerised Per 100 Grams Gel.
Electrolyte Na2SO4:	1			
0.0	165	210	2.0	6.280
			20.0	15.645
	1		44.0	17.985
			187.5	19.850
·275	145	190	0.75	3.035
			3.75	11.025
			21.75	18.260
		-6-		23.000
•550	130	160	1.66	6.315
			5.00 21.5	18.290
			161.25	22.870
-825	105	140	1.0	5:595
	1 3	-4-	4.75	13.100
			21.25	18.250
			161.0	22:190
1.375	67	90	2.0	10.055
			4.25	12.575
			23.5	18.045
Electrolyte NaCl:			143.5	21.990
•				
1.14	140	157	2.0	13.626
			5.5	14·558 18·824
	į		22.5	22.882
	0-	0.5	263.5	8.629
3.42	85	95	1.75	13.476
			5.0 18.75	17.934
			119.75	21.396
4.56	50	65	1.0	7.468
7 3-	, ,	, ,,	2.5	10.813
			20.5	16.344
			140.5	18.812

TABLE II .- continued.

Added Salt Concentration Per Cent.	Setting Time in Secs.	Induction Period in Secs.	Time in Hrs. After Setting.	Wt. of Liquid in Grams Synerised Per 100 Grams Gel.
Electrolyte KCl:				
1.075	112	140	2.0	8.625
20		•	5.0	12.585
			24.5	17.905
			144.0	20.565
2.15	85	95	1.0	7.840
3		,	2.0	11.340
			20.0	19.275
	1		164.75	23.065
3.225	63	75	1.5	8.500
0 0		,,,	2.5	10.210
			23.5	17.815
			167.25	20.440
Electrolyte $K_2SO_4$ :			, ,	
0.39	126	160	2.0	10.305
•-			21.0	18.608
	1		45.0	20.703
	1		211.0	22.789
·78	100	120	1.0	6.676
•	1		2.0	9.735
			20.0	17.742
			120.0	20.355
1.17	80	95	2.0	7.016
•	1		21.0	16.614
			164.0	20.049
1.56	60	68	1.5	6.745
-	1		20.5	15.853
	1		46.0	17.210
			165.5	19.148
	1		1	1

### Discussion of Results.

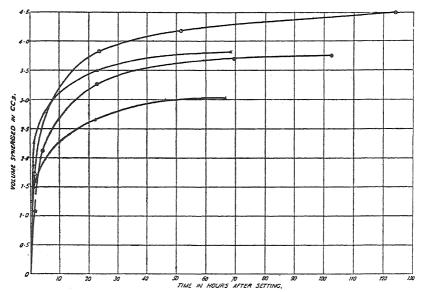
The above results show that the effect of comparatively small quantities of neutral electrolytes on the progress and rate of syneresis is not of a high order of magnitude. At first the initial velocity of exudation and the total quantity of liquid synerised increases with increasing concentration of electrolyte. This occurs up to a certain salt concentration after which further additions of electrolyte bring about a decrease in the quantity of syneretic liquid. This is shown graphically in Fig. 1, which is a typical example of the results obtained. The effect is more pronounced with the sulphates than with the chlorides while the potassium salt is more potent than the corresponding sodium salt.

A similar effect is observed in some of the results obtained by Prakash and Dhar <sup>3</sup> on the effects of electrolytes on the syneresis of goats' blood, although in their paper the authors come to the general conclusion that the syneresis is decreased as the electrolyte concentration is increased. Table III. is reproduced from their results.

A similar result is given for sodium acetate while other instances of an increase of the initial velocity of syneresis up to a maximum value are given.

Although, as stated below, the effect of neutral salts on syneresis is not very pronounced yet the reverse is true concerning the setting time

and the period of induction. Both these quantities rapidly decrease with increasing electrolyte concentration. This is shown graphically



in Fig. 2. The influence exerted by the salts are in the order  $K_2SO_4 > Na_2SO_4 > KCl > NaCl$ .

These results agree in part with those found by Prasad and Hattiangadi 4 on the effect of addition of extra electrolyte to silica

TABLE III.—Influence of Sodium Tartrate on Syneresis. Concentration of Sodium Tartrate = N

Blood = 230 c.c. Total volume = 250 c.c.

	Amount of Syneresis with c.c. of Sodium Tartrate.			
Time,	o c.c.	2 c.c.	4 c.c.	6 c.c.
30 mins	6 64 77 82 92 106 111	34 62 77 84 93 102 105	42 67 80 86 94 107 113	32 52 66 74 80 91 93 113

gels prepared by the action of ammonium acetate on sodium silicate. With such gels they also found that the setting time decreased with increasing salt concentration but the order for the anions used was  ${\rm Cl} > {\rm NO}_3 > {\rm SO}_4$ .

<sup>&</sup>lt;sup>4</sup> Prasad and Hattiangadi, J. Ind. Chem. Soc., 7, 341, 1930.

The general conclusion which may be drawn from this work is that the presence of comparatively low concentrations of neutral electrolytes do not exercise a very pronounced influence on the phenomenon of

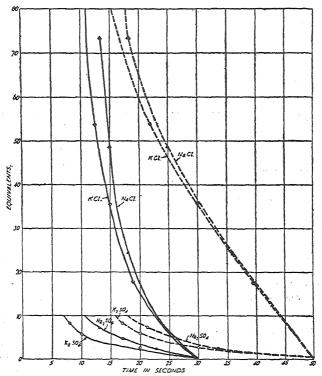


FIG. 2 EFFECT OF ELECTROLYTES ON SETTING TIME AND INDUCTION PERIOD.

KEY,- \_\_\_\_\_\_SETTING THE, \_\_\_\_\_\_INDUCTION PERIOD.

syneresis. The main effect is the increase in the velocity of coagulation which is reflected in the decrease both of the setting time and the period of induction.

### Summary.

The effect of the presence of small quantities of electrolytes on the phenomenon of syneresis has been studied.

It has been found that the main effect is an increase in the velocity of coagulation.

The author wishes to express his thanks to the Director of Building Research for kind permission to publish these results.

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## THE CATALYSIS OF GASEOUS REACTIONS BY CHLORINE.

By S. BAIRSTOW.

Received 3rd August, 1933.

The catalysis of various gaseous reactions by iodine has now been fairly extensively investigated, and it is of some interest to examine the catalytic influences of the other halogens. This note describes certain observations on catalysis by chlorine; from these further conclusions about the mechanism of the process may be drawn.

The decomposition of diethyl ether is catalysed by chlorine, and the ratio:

(rate with 6.7 mm. chlorine)/(rate without chlorine) for 150 mm. ether at 463° C. is about 20. The corresponding ratio for the corresponding iodine catalysis is 120, and thus chlorine is only about one-sixth as effective as iodine at this temperature. By measurement of the initial rate of reaction for different initial pressures of ether it is found that the reaction is of the first order with respect to the ether. The rate is also directly proportional to the chlorine concentration. The whole course of the reaction, however, does not conform to a definite order since the catalyst concentration changes during an experiment. This is due to the fact that some of the catalyst is used up in a chemical reaction during the decomposition, as can be shown by allowing the catalysed decomposition to attain completion and then adding a further quantity of ether. The new rate, although much greater than that of the uncatalysed decomposition, does not correspond to the full original amount of chlorine.

At all stages the reaction is much faster in presence of chlorine than in its absence, so that there is no doubt that free chlorine is present all the time.

The following conclusion is important: it was possible to argue that the catalysis by iodine involved the following definite chemical reactions:—

$$\begin{array}{c} {\rm C_2H_5\,.\,O\,.\,C_2H_5 +\,I_2 = C_2H_5I + HI + CH_3CHO} \\ {\rm CH_3\,.\,CHO +\,I_2 = CH_3I + HI + CO} \end{array}$$

followed by

$$C_2H_5I + HI = C_2H_6 + I_2$$
  
 $CH_3I + HI = CH_4 + I_2$ .

Now at the temperature of working, if hydrogen chloride were formed in this manner, the regeneration of chlorine would not be possible. Therefore, if catalysis by chlorine proceeded in this manner, a mixture of 10 mm. chlorine and 200 mm. of ether would show a rapid increase in pressure of 10 mm. and then the rate would fall to that of the uncatalysed reaction. Actually the whole reaction, involving a pressure

increase of about 175 mm., is catalysed right to its end. Thus the purely chemical theory is quite untenable, at least in the case of chlorine, and therefore it is improbable for the case of iodine. Since on other grounds it was regarded as unnecessary, the theory can be dismissed

completely.

The action of chlorine on the decomposition of trimethylamine and of methyl ethyl ketone—two reactions which are relatively insensitive to the catalytic influence of iodine—was investigated. The object was to see whether a halogen with a higher heat of dissociation, and therefore capable of containing more vibrational energy, would be effective in cases where iodine failed. Actually the results were negative, since the effect of chlorine on trimethylamine is normal—i.e., the increase in rate is about one-quarter that produced by iodine, -and the addition of as much as 60 mm. chlorine to 100 mm. methyl ethyl ketone only multiplies the rate by a factor of about three.

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### THE SWELLING OF PROTEIN FIBRES. PART II. SILK GUT.

By D. JORDAN LLOYD AND R. H. MARRIOTT.\*

Received 4th August, 1933.

Silk has been described by Astbury (1932)<sup>1</sup> as the ideal protein since the polypeptide backbone of the molecule lies in the fully extended condition and the R groups or side chains are, for the most part, short The molecules of silk should, therefore, be capable and non-polar. of very close lateral packing when built up into the silk fibre; lateral cohesive forces might be anticipated to be very high and the power of swelling of the fibre correspondingly low. Silk threads have a considerable tensile strength (Mark, 1932)2 and have long been recognised as having hygroscopic properties (Denham and Lonsdale, 1932).3 The cohesive forces between the molecules are, therefore, high but at the same time channels must exist into which water molecules can penetrate. Silk, in passing from a dry atmosphere to one fully saturated with water, shows a lateral swelling of about 16-18 per cent. of the original diameter and an increase in length of about 1.3 per cent. (Denham and Dickenson, 1932).4 The volume increase of a cylinder of silk, in passing from the dry to the wet state, may, therefore, be calculated roughly as 40 per cent. The increase in weight has been found experimentally to be about 33 per cent. (Jordan Lloyd and Phillips, 1932). The absorption of water into the silk fibre leads to some loss of tensile strength.

The molecule of silk is built up mainly from glycine, alanine, and,

<sup>\*</sup>From the Laboratories of the British Leather Manufacturers' Research

<sup>&</sup>lt;sup>1</sup> Astbury, Trans. Faraday Soc., 29, 193, 1932. <sup>2</sup> Mark, Trans. Faraday Soc., 29, 6, 1932. <sup>3</sup> Denham and Lonsdale, Trans. Faraday Soc., 29, 305, 1932. <sup>4</sup> Denham and Dickenson, Trans. Faraday Soc., 29, 300, 1932.

<sup>&</sup>lt;sup>5</sup> Jordan Lloyd and Phillips, Trans. Faraday Soc., 29, 132, 1932.

to a less extent, tyrosine. It is, therefore, compared with other proteins, not only almost free from those R-groups which could form co-ordinate links with water molecules  $(-OH, -NH, -NH_2)$  but also from those which could act as charged centres  $(-NH_3^+$  and  $-COO^-)$ (Jordan Lloyd and Phillips, 1932). Brill (1923) 6 has brought forward evidence that in the silk molecule glycine and alanine residues alternate. If a three-dimensional atomic model be built on these lines, it can be seen that the arrangement of the different atoms in the molecule is not symmetrical about the molecular axis; in other words, the molecule has a back and a front and right and left sides. Fig. 1 (a) and (b) shows two diagrammatic representations, roughly at right angles, of a polypeptide chain built up from glycine and alanine in alternating sequence.

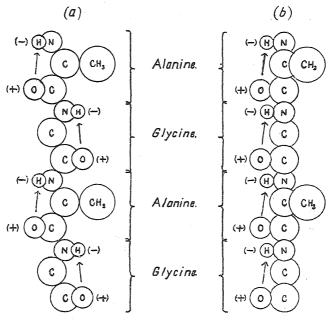


Fig. 1.—With the exception of those of the imino groups all H atoms have been omitted from the diagram.

The most striking fact that emerges is that if the molecular backbone is lying at its fullest extension as a simple zig-zag, all the carbonyl oxygen atoms and imino hydrogen atoms lie on the same side and roughly in the same plane (Fig. 1 (b)). Since a sharing of electrons probably occurs between these two groups, they will show residual polar forces, the oxygen atoms being positively and the hydrogen atoms negatively charged (Jordan Lloyd, 1932).7 One face of the molecule, therefore, is made up of a regular mosaic of weak positive and negative polarities, while the opposite face, formed of the C and N atoms of the backbone, is completely non-polar. Since the R-groups of alanine and glycine are both short, two adjacent silk molecules can be placed in close contact along their backbones, either at their polar or at their non-polar faces.

Brill, Annalen, 434, 204, 1923.
 Jordan Lloyd, J. Soc. Chem. Ind., 51, 141 T, 1932.

Fig. 1 also shows that all the methyl groups from the alanine must lie on one side of the molecule and all the R-groups from the glycine (which are simply hydrogen atoms) must lie on the other (Fig. 1 (b)). molecules can, therefore, be packed in at least two ways with nonpolar groups touching, namely the non-polar -C-N-N- chain or the methyl groups. Van der Waal's forces will, therefore, exert an influence in holding the structure together but certainly residual polar forces will also play an important part. It is also possible that between two adjacent molecules there may be a donation of electrons from the oxygen of the carbonyl group to the hydrogen of the imino group, thus forming a co-ordinate link (Jordan Lloyd and Phillips, 1932). In any case, if such molecules are packed closely into bundles to form a fibre. they will not pack up to form a cross-section of uniform pattern like a bundle of equal cylindrical rods but will form packets in which every molecule has a definite orientation with respect both to the axis and to the cross-section of the fibre and these packets will then pack together according to a second system of orientation, the whole fibre conforming to Astbury's description, namely "a self-contained system riddled through and through by crystallisation faults" (Astbury, 1932). The forces across the faults (or planes of cleavage) will differ, however, both in strength and character. The structural pattern of the silk fibre will be more complicated than suggested by the simple diagrams in Fig. 1, since other units besides glycine and alanine are present, tyrosine, for instance, forming about 10 per cent. of the molecule (Fischer and Skita, 1901: 8 Abderhalden and Behrend, 1909).9 The fundamental principles of the structure will, however, be the same and the silk fibre should be capable of being broken up into fine fibrils by any substance capable of attacking the crystal at its "faults." Different reagents may be expected to attack different "faults" in the structure and to influence the properties in different ways.

The swelling of a dry silk fibre in water or water vapour must depend in the first place on the passage of water into the fine capillary spaces in the structure. Since the extent of swelling is always controlled by the balance between the solvent pressure of the water, causing diffusion into a system, and the cohesive forces of the system, which resist any extension in volume, the capacity of the silk fibre to absorb water should be increased by any reagent which, by attacking the structure at its planes of cleavage, weakens the cohesive forces. The influence of hydrochloric acid, sodium hydroxide, chloride and nitrate, lithium iodide, urea and thiourea on the swelling of silk fibres are described below, together with their effect on the micro-structure and birefringence.

The form of silk fibre taken for the experiments was silk gut prepared for surgical sutures. This material is obtained by dissecting out the silk sac of the silk worm and extending it. The liquid silk from the sac coagulates and forms a thread which undergoes further slow stretching as its drying is completed. The thread obtained in this way consists of pure fibroin. The diameter is about 0.4 mm. and the thread is sufficiently stout to form a convenient material for weighing. Although the diameter of the thread is of such dimensions that the area of surface per unit weight of silk is very much less than in the case of the naturally extruded silk filament, yet the fibres still have a sufficiently

<sup>&</sup>lt;sup>8</sup> Fischer and Skita, Z. physiol. Chem., 33, 177, 1901. <sup>9</sup> Abderhalden and Behrend, Z. physiol. Chem., 59, 236.

high ratio of surface to volume to cause errors in weighing when they are taken out of a solution, blotted and weighed. These errors are of the order of  $\pm 2.5$  per cent. The slight fluctuations in weight recorded by Denham and Dickenson as occurring after 6 days between  $p_{\rm H}$  I and  $p_{\rm H}$  5 would, therefore, fall within the experimental error.

Preliminary experiments already published (Jordan Lloyd and Phillips, 1932) and further experiments summarised in Table IV. show that in water or hydrochloric acid in concentrations up to N/10 or in twice molar solutions of salts, equilibrium was attained in 24 hours at 18° and maintained for 3 weeks. In sodium hydroxide solutions, except those as dilute as N/1000 or less, equilibrium was never attained, swelling being progressive with time. For this reason 24 hours was taken as a sufficient length of time for most of the experiments, which were carried out at a uniform temperature of 18° unless otherwise stated.

### Influence of the External $p_{\rm H}$ over the Range 0.3-13.

Fig. 2, curve (a) shows the curve of swelling obtained in this way over a  $p_{\rm H}$  range of 0·3-13. The experimental points show the swollen weight at the different values of  $p_{\rm H}$  calculated as a percentage of the weight after drying at 100°. The curve is in striking contrast to that obtained for collagen fibres (Jordan Lloyd, Marriott and Pleass, 1933). The conspicuous peak of acid swelling is absent and the curve, as a whole, is flat



Triangles = curve (a); squares = curve (b); circles = curve (c), crosses = curve (d): Note that curve (d)coincides with curve (a):

#### FIG. 2.

with a slight tendency to rise at  $p_{H}$  values < 1 and a marked tendency to rise at  $p_{\rm H}$  values > 11. It will be shown later that the alkali causes the fibre to split up into a number of fine fibrils and there is no doubt that the increased swelling in alkaline solutions is due to the action of the alkali in weakening the cohesive forces of the fibre. If the silk be left in contact with the alkali for a further length of time, alkaline swelling will make itself apparent at lower values of  $p_H$ . Denham and Dickenson (1932) have shown that with natural silk filaments after 6 days it is even apparent at all values of  $p_{\rm H} > 5$ . The permanent nature of the alkali effect can be shown by swelling in alkali, washing free from alkali and then again taking the  $p_{H}$ -swelling curve. Fig. 2, curve (b), was obtained by using silk gut which had been treated for 24 hours with 0.075 N NaOH  $(p_{\rm H}=13.0)$  and washed free from alkali. The striking feature of the curve is that the alkali treatment has had the effect of increasing water absorption by the silk gut at all values of  $p_{\rm H}$ . The slightly lower values obtained between  $p_{\rm H}$  12 and 13 are probably due to a slight solution of the silk. Curve (b) is similar in general form to curve (a). No maxima of acid or alkaline swelling are to be seen. Curve (c) was obtained by using silk gut which had been treated for 24 hours with 0.5 per cent. Na2S. 9H2O in a borax buffer mixture at  $p_H$  11.1 and washing free from reagent. The solution was made by mixing 280 c.c. of a I per cent. solution of borax; 120 c.c. of N/10 NaOH and 40 c.c. of a 5 per cent. solution of Na<sub>2</sub>S. 9H<sub>2</sub>O.

<sup>10</sup> Jordan Lloyd, Marriott and Pleass, Trans. Faraday Soc., 29, 554, 1933.

This solution will reduce the sulphur linkages in keratin and has a strong effect on the swelling of hair. On silk gut, however, though it does lead to subsequent increased swelling at all values of  $p_{\rm H}$ , its effect is only commensurate with its alkalinity, *i.e.*, it is less than that of NaOH at  $p_{\rm H}$  13.

It has already been mentioned that alkaline solutions lead to the appearance in the silk fibre of fibrils which are readily separated by slight mechanical pressure. There is no doubt, therefore, that alkali brings about a weakening of the lateral cohesive forces and that the effect is not reversed by washing out the alkali.

Curve (d) shows the effect on the swelling of silk fibres of a pre-treatment of the silk with 4N HCl. Curve (d) lies coincident with curve (a). This reagent also causes a splitting of the silk fibre though greater mechanical pressure is needed to tease out the fibrils than in the case of the alkalitreated hair. The acid pre-treatment, however, has had no effect on later swelling. The effect of the acid, therefore, is much more readily reversed than that of the alkali and the splitting into fibrils probably takes place at a different plane of cleavage.

## Influence of Concentrated Solutions of Hydrochloric Acid and Sodium Hydroxide.

Since concentrated solutions of these reagents reduce the tensile strength of the silk to such an extent that the threads become difficult to handle without breaking and impossible, therefore, to dry and weigh accurately, their influence on the swelling was followed by observing the changes in length, diameter and microscopical appearance of silk fibres. Length was measured with a millimetre rule and diameter with calipers. The order of accuracy of the measurements is not high, and may be taken as  $\pm$  5 per cent. The reagents are substantially without effect on the length of the fibre but the effect on diameter is considerable. Table I. gives a summary of the results.

It can be seen that the structure of the fibres gives way under the action of the reagents and that acid and alkali act differently. In alkali, the fibre maintains its length unchanged but the swelling is greater than in water and is brought about by a progressive increase in diameter. This lateral expansion is accompanied by the appearance of separate fibrils in the fibre and the silk becomes soft and gelatinised in the alkaline solutions, a condition which suggests that the protein has become hydrated. It has already been suggested (Jordan Lloyd and Phillips, 1932) that a rupture of co-ordinate links between two parallel polypeptide chains under the action of alkali is a possible basis of a change of this type:—

The weakening of the lateral forces causing the appearance of fibrils is apparent in 0.5N and N sodium hydroxide. In stronger solutions, 2N to 8N, the cohesive forces along the fibre axis also give way and some

TABLE I.

Reagent.		Per of Ir Diar	th as Cent. nitial neter Dry.	Condition.		Microscopical Appearance.	
		Day.	10 Days.	r Day.	10 Days.	r Day.	
Wate	r	116	118	Rigid	Rigid	Longitudinal striations visible but too hard to	
o-5N	NaOH	140	175	Fairly rigid	Fragile	penetrate with needle. Fine longitudinal stria- tions; splits with needle into fibrils from 0.5 to	
$_{1}N$	,,	155	190	Still fairly rigid	Fragile	20μ. Splits easily into fibrils	
2 <i>N</i>	,,	167	180	Soft and fragile	Very fragile	about 0.5 \( \mu\) in diameter. Soft, breaks transversely on touching into short lengths of parallel fibrils.	
4N	,,		194	Very fragile	Very fragile	lengths of parallel fibrils. Soft, breaks transversely on touching into short	
6N	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	_	170	Very fragile	Very fragile	lengths of parallel fibrils. Soft, breaks transversely on touching into short lengths of parallel fibrils.	
8N 10N	,,	136	thin thin	Very fragile Fairly rigid	Very fragile Fraying into fine fibrils. Very fragile when	Rather more powdery. Hard, except on outside, which tends to fray off under rolling pressure into acicular fibrils.	
o∙5N	HCl	110	114	Rigid	touched Rigid	Longitudinal striations. Hard but can just be teased into fibrils about	
ıN	,,	_	117	Rigid	Rigid but splits into fibrils under	o·3µ in diameter.  Hard but can be teased into fibrils.	
2 <i>N</i>	,,	123	140	Rigid	pressure Rigid but splits into fibrils under pressure Very faintly	Hard but splits and breaks into needles.	
4N	,,	126	138	Rigid	mauve Rigid but powders under pressure Faintly mauve	Softer; splits easily into short needles.	
6N	"	129	188	Fairly rigid	Fragile and soft, purple	Soft; breaks up easily into short needles.	
8 <i>N</i>	,,	200		Soft, fragile, pale	Dissolving, purple	Very soft; crushes.	
10N	,,			purple Dissolved, giving purple solution			

hydrolysis undoubtedly occurs. Swelling and water absorption reach a maximum at about 4N to 6N. In stronger solutions, the silk resists the reagent for a rather longer time and is apparently less hydrated. It is interesting however, to note that though the fibre breaks up under slight mechanical disturbance in concentrations of 2N and upwards, only in 10N and after ro days did it show spontaneous splitting into fibrils visible to the naked eye. Swelling never exceeds 200 per cent. of the original diameter, which, assuming constant length and a density approximating to unity, means that the maximum swollen weight is 400 per cent. of the initial dry weight. The silk fibre can, therefore, by weakening its structure with alkali, be made to take up three times its weight of water. Although no significant change in length occurs during this process, the tensile strength falls nearly to zero.

Immersion in solutions of hydrochloric acid also brings out indications of fibrillar structure in the silk gut, although very little teasing out of fibrils can be effected at concentrations below about 1 oN. At concentrations between this value and about 4N the fibres can be teased into fibrils with increasing ease, but these show no evidence of becoming gelatinised nor is the swelling conspicuously greater than in water. Above this concentration, however, considerable swelling progressive with time occurs

and the fibre becomes soft and gelatinous.

In the acid solutions, the tensile strength does not fall so rapdily with increasing concentration of reagent as is the case in alkaline solution. In 10N hydrochloric acid, the silk turns purple and dissolves in a few hours at laboratory temperature. Very concentrated acid, therefore, breaks both lateral and axial links and has as well a chemical action on the silk fibroin. This development of colour can be observed in less concentrated solutions, the rate of development of the colour being slower in the weaker solutions—a faint colour can be observed with 0.2 N HCl after 9 days.

### The Influence of Acid and Alkali on the Birefringence of the Fibres.

Silk fibres have a high birefringence. Measurements of this have been carried out in order to follow the effect of acids and alkalies. The method employed was to mount the fibre, after treatment, in the experimental liquid, and to compensate the double refraction by inserting a quartz wedge. The thickness of quartz required to achieve this was measured and calculated as the retardation in millionths of a millimetre  $(\mu\mu)$  produced by the difference in refractive index of the extraordinary and ordinary ray. A measurement of the diameter of the fibre was also made and on the assumption that the fibre was substantially circular in cross-section, the birefringence was deduced from a Michel-Lévy chart of birefringences (Johannsen, 1918).<sup>11</sup>

In the first series of experiments, silk gut was used but owing to the thickness of the fibre the polarisation colours were of too high an order to be compensated by the quartz wedge employed. Where, however, the fibre had broken down or could be teased out by means of needles, it was possible to determine the birefringence and to show that solutions of increasing concentration of sodium hydroxide diminished the birefringence. A supply of raw silk was, however, kindly supplied by Dr. Denham. This was freed from the sericin or silk gum by the method of Denham and Dickenson (1932). The filaments were found to be generally about 10 to 15  $\mu$  in diameter (average about 13·5  $\mu$ ) and gave polarisation colours of the first order.

Since, as has been indicated, the action of the reagents on silk is, for the most part, a progressive one, the determination of the double refraction was made after 20 to 24 hours' treatment. A number of determinations

<sup>&</sup>lt;sup>11</sup> Johannsen, Manual of Petrographic Methods, 1918 (New York).

was made for each lot of silk, the particular fibres examined being chosen at random, the only criteria being that under crossed nicols the fibre should show an even polarisation colour and that it should be reasonably straight for about 50 to 100  $\mu$ . The measurement was not always easy and the extent of the variations is indicated in the series of values shown in Table II.

TABLE II.

Reagent.	Diameter of Fibre, μ.			Diameter of Fibre, µ	Retar- dation, μμ.	Average Retarda-	
Water	18 13 10 10 10 12 13·9 16 16 15 14 18	322 658 504 511 406 560 455 532 378 448	477	o∙o75N NaOH	22 13 12 15 12 15 12 22 22 average 13 14 16 15	427 259 455 441 252 336 322 301 553 441	379
4N HCl	15 13 10 15 12 13 12 13 12 13 12 13 13 12 18 13	350 511 217 546 420 189 385 441 693 203	400	1·25N NaOH	24 23 18 22-3 24 22 23	301 322 343 315 322 336	323

In making use of the figures, it should be borne in mind that the birefringence takes into account the thickness of the fibre. Thus a fibre 10  $\mu$  in thickness and with a retardation of 400  $\mu\mu$  has a birefringence of 0.040 and if this fibre is swollen to 20  $\mu$  diameter and there is no loss of double refraction, the birefringence will fall to 0.020. Thus an alteration in the birefringence may be due to a swelling action which does not affect the refractive indices or to an alteration in one or both of the refractive indices. Both effects may indeed be operating. On the other hand, a change in the interference colours, i.e., the retardation, definitely indicates a change in one or both of the refractive indices, provided there is no alteration in the actual amount of substance through which the light is transmitted or in the direction of the light relative to the optic axis.

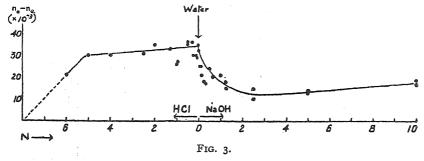
It would appear that silk possess a birefringence of about 0.032 to 0.035, as determined by means of a quartz wedge compensator, variations being found between different filaments. Direct determination of the two refractive indices using the immersion method indicates that  $n_{\rm e}={\rm slightly}$  less than 1.550 and  $n_{\rm e}={\rm I}.580$  (approx.), giving a birefringence of about 0.030. The optical determinations were all carried out using a half watt pearl lamp, a suitable source of monochromatic light not being available, and they are not, therefore, more accurate than about  $\pm$  0.002.

The birefringence of the silk filaments shows a rapid fall with increasing concentration of sodium hydroxide whereas in hydrochloric acid solutions up to concentrations of about 5N only a slight fall occurs. At about 5N HCl, the birefringence falls, the filaments dissolving completely in

8N HCl in 24 hours at laboratory temperature (Fig. 3). The experimental points suggest that between water and 2N HCl the birefringence alters somewhat erratically. Similar erratic variations occur on the alkaline side, *i.e.*, up to concentrations of about N NaOH. Duplicate experiments suggest that these variations are real, but for the present they have been neglected and a smooth curve drawn through the points. It would appear definite, however, that the birefringence is greater in 10N NaOH than in about 2.5N NaOH, the birefringence being at a minimum at about 2.5 to 3.0N NaOH.

When the retardation is plotted against the normality of the solutions, the curve obtained is similar to that showing the variation in birefringence, the erratic changes occurring in the range between 2N HCl and N NaOH being again observed. This similarity strongly suggests that the reagents are affecting the structure of the filaments and not merely causing imbibition of water.

The effect of another alkali, namely calcium hydroxide in saturated solution was examined. Treatment of the silk gut with a suspension of calcium hydroxide in water slightly softens it so that it can then be teased out into fibrils. This action produces only a very slight fall in the birefringence, the value obtained being about 0.030, whereas with sodium hydroxide at similar concentration (N/20) the birefringence falls to 0.026.



The study of the birefringence shows that alkalies attack the structure of the silk more readily than acids, except in very concentrated solutions. It has previously been shown (Kaye and Jordan Lloyd, 1924)<sup>12</sup> that isolated collagen fibres, when swollen with either acid or alkali (in which condition they shorten in length), lose their double refraction. This loss can, however, be prevented by keeping the fibre under external pressure or restored either by tension or removal of the acid or alkali, methods which remove the water of osmotic swelling (Marriott, 1932).<sup>13</sup> The loss of birefringence in collagen fibres is, therefore, a structural change but not necessarily identical with the change brought about in the silk fibre.

# The Influence of Acid and Alkali on the Structure of the Fibres as Revealed by X-Rays.

By the courtesy of Dr. R. H. Pickard, F.R.S., the silk fibres were examined under X-rays. The examinations were made by Mr. M. O. Pelton of the Shirley Institute. Four threads were submitted for examination: the first had been soaked in water; the second had been soaked for 24 hours in 0.075N NaOH and then washed free from reagent—as shown above this treatment causes the appearance of fibrils and has a permanent influence on the swelling of the fibre; the third had been soaked for 24 hours in 4N HCl and then washed free from reagent—as shown

Kaye and Jordan Lloyd, Proc. Roy. Soc., 96B, 293, 1924.
 Marriott, Biochem. J., 26, 46, 1932.

above, this treatment enables the fibre to be teased into fibrils but does not have any influence on later swelling. These three threads were submitted to X-ray examination in the water-swollen condition but dried up during the exposure of the photographic plate. The fourth thread had not been treated in any way and was exposed in the dry condition. All four threads gave identical X-ray diagrams. Any change which had been brought about by the reagents, therefore, had not affected the structure

TABLE	III.

Reagent.	Average Birefringence.	Average Retardation (μμ).	Reagent.	Average Birefring- ence.	Average Retarda- tion (μμ).
8 N HCl 6 N ,, 5 N ,, 4 N ,, 2.5 N ,, 1.25 N ,, 1.00 N ,, 0.5 N ,, 0.125 N ,,	Dissolved  0.021  0.030  0.031  0.035  0.035  0.036  0.036  0.036  0.036  0.030  0.036  0.030  0.032	Dissolved  330  426  400  384  450  424  330  359  453  495  385  415  396  335  477  424	10 N NaOH  5 N ,,  2.5 N ,,  1.25 N ,,  1.0 N ,,  0.625 N ,,  0.312 N ,,  0.156 N ,,  0.075 N ,,  0.050 N ,,	\[ \begin{array}{c} \cdot \cdo	224 \ 223 \ 207 \ 268 \ 151 \ 323 \ 273 \ 305 \ 3379 \ 284 \ 397 \ 379 \ 411

of the crystal units or micelles in the fibre. The acid or alkali, therefore, can be regarded as causing a splitting of the fibre by influencing the intermicellary forces and the water which passes in during swelling is, in all three cases in the inter-micellary channels of the fibre. The evidence of the X-rays quoted above suggests that in the case of silk, the loss of birefringence in the limits of 4N HCl to 0.075 NaOH is due to the splitting of the fibre into fibrils by inter-micellary cleavage.

### The Influence of Hydrating Salts, Urea and Thiourea.

Salts from the one end of the Hofmeister Series have long been recognised to have a swelling effect on proteins. This swelling is not to be attributed to the establishment of a Donnan equilibrium or to any other form of osmotic effect but is due to a dispersion of the protein through a weakening of the cohesive forces between the protein molecules (Jordan Lloyd and Phillips, 1932). Katz (1932)<sup>14</sup> has also shown that substances such as urea and thiourea in concentrated solution have a swelling action on gelatin and he attributes this to the formation of a complex with the gelatin which leads to an increase of the bound water.

The effect of these substances on silk fibres is interesting. They certainly lead to a slight increase in the amount of water absorbed by the silk and bring about a certain amount of coarse splitting of the fibre, but they neither produce the fine fibrils characteristic of acid or alkaline swelling

<sup>14</sup> Katz, Trans. Faraday Soc., 29, 279, 1932.

nor do they materially affect the birefringence of threads. Probably the reagent diffuses into the fine channels of the fibre and becomes adsorbed at internal surfaces and increases the amount of bound water of the system. Table IV. gives a summary of experimental results.

TABLE IV.

The second secon	Weight as Per Cent. of Dry Weight.			
	Day.	Days.	20 Days.	Condition after 1 Day at 18°.
Water at 18°	132	135	133	Hard, cannot be teased into fibrils.
2M NaClat 18°	135	134	135	
2M NaNO <sub>3</sub> at 18°	136	136	136 136	
., ., 37°	138	138	138	
214 Lil at 18°	157	157	-	Hard but can be teased into
$2M$ ,, $37^{\circ}$	162	162	_	coarse fibrils about 300 $\mu$ in diameter.
Urea (sat. soln.) at 18° .	191	193		Hard but can be teased into
,, ,, ,, 37° ·	-	-	-	coarse fibrils about 50µ in diameter. Birefringence about
Thiourea (sat. soln.) at 18°	152	153	_	0-035. Very like urea.
" " " 37°	147	140		

Prolonged boiling in nearly saturated solutions of sodium iodide or nitrate leads to a dispersion of the silk threads. The first sign of change is that the threads contract to about half their previous length and increase in diameter. This is the only condition so far observed which produces any noticeable change in the fibre length.

#### Discussion.

The investigations on the swelling of silk show that it is impossible to discuss any theory of protein swelling without taking into account the influence of structure. The fibrillar structure of the silk fibre is interesting. In the silk filament spun by the silkworm from the fluid silk of the silk sac, the heterogeneously arranged molecules are oriented by the streaming of the silk as it is spun. In silk gut prepared artificially, the same orientation of the molecules occurs, the plastic flow producing a fibrillar structure. Structures of this type are well known in naturally occurring materials of biological origin, such as the collagen fibres of the connective tissues in animals or the hairs of the cotton seed, but their existence in silk threads shows that their formation does not depend so much on the special forces of growth as on the fundamental properties of the molecules involved. This possibility has been pointed out by Sir William Bragg (Nature, 1933). 15

The swelling of dry silk in water vapour is a function of the vapour

The swelling of dry silk in water vapour is a function of the vapour pressure and the fact that the curve of swelling in vapour rises smoothly, until at saturated vapour pressure it reaches the same level as in liquid water, shows that swelling in water is an imbibitional process. The swelling of silk in dilute acids or alkalies does not show any increased

rise above the level in water and it may, therefore, be inferred that "osmotic" swelling, so characteristic of gelatin jellies and collagen fibres, does not occur. Since "osmotic" swelling is due to the formation of ionisable salts between the non-diffusible protein and the diffusible electrolyte with the consequent establishment of a Donnan equilibrium, its absence in silk fibres is not surprising. In the first place, silk contains few constituents likely to give rise to charged centres where salt formation would occur; Vickery and Block (1931) 16 give about I per cent. as the concentration of the bases in a hydrolysate of silk fibroin (arginine, 0.74 per cent., lysine, 0.25 per cent., histidine, 0.07 per cent.), and Abderhalden and co-workers give figures varying from 1-4 per cent. with the different classes of silk for the di-carboxy acids (Abderhalden and Behrend, glutamic acid, o per cent., aspartic acid, 0.75 per cent. for Canton silk fibroin; Abderhalden and Spack (1909), 17 glutamic acid, 1.0 per cent., aspartic acid, 2.5 per cent. for Indian tussore fibroin. Moreover, as Donnan has pointed out (1933) 18 the conditions of equilibrium will not be entirely the same in a structureless system and a highly structural one such as a fibre (see also Jordan Lloyd, 1932).

The action of concentrated acids, of alkalies, salts and urea in raising the level of swelling above that in water is not due to any increase in the internal osmotic pressure of the system, but is due to a weakening of the cohesive forces of the fibre-structure. Under the microscope, this effect shows itself by a separation into fibrils in every case where swelling is increased above the equilibrium level for water. The evidence of the X-rays suggests that treatment with acid and alkali sufficient to cause the appearance of fibrils is not enough to influence the structure of the crystal units. The evidence of birefringence suggests that the treatment with the reagents causes a spreading out of the substance of the filaments, *i.e.*, an increase in inter-micellary volume.

The evidence given above suggests that in all cases where equilibrium is attained, the swelling, whether in water, acid, alkali, salt or other solution, is purely imbibitional. Alkalies at all concentrations appear to lead to a hydration of the protein, and both alkalies and concentrated acids have a progressive effect on swelling that can safely be attributed to a hydrolysis of the fibroin with hydration of the degradation products.

#### Summary.

1. Silk fibres (fibroin) absorb water to the extent of about 30 per cent. of their dry weight from water and many aqueous solutions.

2. Silk fibres do not increase their water content in acid or alkaline

solutions by the establishment of a Donnan equilibrium.

- 3. In sodium hydroxide solutions more concentrated than N/100, silk fibres swell slowly and continuously, the rate and extent of the swelling being proportional to the concentration of the alkali up to a concentration of about 6N. In even more concentrated solutions, the swelling is less than the maximum. The swelling is accompanied by a splitting of the fibre into fibrils about  $0.5~\mu$  in diameter and by a softening of the protein.
- 4. Preliminary treatment with alkali leads to greater absorption of water under all conditions.
- 5. It is suggested that in the first place alkaline swelling is due to a non-reversible opening of a co-ordinate link between the carbonyl group of one peptide chain with the imino group of an adjacent parallel chain with

18 Donnan, J. Inter. Soc. Leather Trades Chem. 17, 136, 1933.

 <sup>16</sup> Vickery and Block, J. Biol. Chem., 93, 105, 1931.
 17 Abderhalden and Spack, Z. Physiol. Chem., 62, 131, 1909.

a binding of water molecules at the two groups released. Further swelling is probably due to slow hydrolysis and disintegration of the structure.

6. In hydrochloric acid solutions less concentrated than 2N, the fibres remain rigid but can be broken by mechanical pressure into fibrils about  $0.3 \mu$  in diameter. These fibrils do not appear to be hydrated to any extent. In higher concentrations the fibres show some swelling progressive with time, they soften and break under mechanical pressure into short needles. At 10N concentration the fibres dissolve in 24 hours.

7. In contact with hydrochloric acid solutions > 0.5N, silk fibroin develops a purple colour, the rate and extent of colour development being

proportional to the concentration of the acid.

8. Preliminary treatment with acid does not lead to increased swelling.

9. It is suggested that in the first place, acid destroys lateral cross linkages but that no water binding follows. Later swelling is probably due to hydrolysis and disintegration of the structure.

10. Salts, urea and thiourea weaken the structure slightly and cause

slight swelling.

II. Silk fibres are strongly birefringent and the birefringence falls off rapidly in alkaline solutions and to a less extent in acid solutions.

12. Treatment of silk with acid or alkali is without effect on the X-ray

diagram.

13. The swelling of silk fibroin under all the conditions investigated is a purely imbibitional or capillary process.

# THE EXISTENCE OF A COMPLEX IN RACEMISING SOLUTIONS.

By Alan Newton Campbell and Alexandra Jean Robson Campbell.

# Received 21st August, 1933.

Previous work 1 has shown it to be very probable that in the catalytic racemisation of tartrates (Rochelle salt) by means of sodium hydroxide, a complex is formed between the sodium hydroxide and the tartrate. In contradistinction to the original dextrorotatory tartrate, this complex is strongly lævorotatory.<sup>2</sup> On the other hand the catalytic racemisation of mandelic acid, which is even more readily brought about by acid or alkali, did not appear to be accompanied by complex formation, so far as the evidence went. The conclusion that catalytic racemisation proceeds via complex formation and that the phenomenon is general, is alluring but it cannot be considered general if no evidence of complex formation in the case of mandelic acid is forthcoming. Complex formation is not the only possible explanation of the catalytic action. It may be that the presence of the catalyst markedly affects the properties of the medium (solvent), for instance, its dielectric constant. To clear up the matter, if possible, it was decided to investigate further properties of alkaline and acid solutions of Rochelle salt and of mandelic acid. A marked departure from additivity increasing with increasing concentration of catalyst, is not necessarily evidence of complex formation; it might equally well be ascribed to progressive change in the nature of the medium. It is necessary also to consider the nature

<sup>&</sup>lt;sup>1</sup> J.A.C.S., **54**, 3834, 4581, 1932; J. Physic. Chem., **36**, 2510, 1932. 
<sup>2</sup> Nature, **129**, 281, 1932.

of the property in question. For example, a markedly increased viscosity over that of the sum of the components accompanied by slight change only in refractive index, might reasonably be supposed to represent complex formation, i.e., increased particle size, in the absence of colloidal particles, micelles, or long chain molecules. On the other hand, a viscosity agreeing fairly well with additivity and a marked deviation from additivity in the refractive index would point rather to an influencing of the properties of the medium.

#### Experimental.

The following properties were investigated: density, viscosity, refractive index, and heat of solution. The technique was that of ordinary good work, e.g., the refractive index was determined in a Zeiss-Pulfrich instrument, through which thermostat water was circulated, and the heat of solution in an electrically heated adiabatic calorimeter. The solutions were always molar with respect to Rochelle salt (anhydrous) and i-mandelic acid and  $M_{l_{10}}$  or  $M_{l_{20}}$  with respect to *l*-mandelic acid, in view of the cost of this substance. The Rochelle salt and i-mandelic acid were purchased and the l-mandelic acid prepared from amygdalin. The sodium hydroxide solutions were prepared by weighing out sodium hydroxide sticks (Mallinckrodt's) and dissolving in water, followed by standardisation. Because of the relatively large quantities of sodium hydroxide solution required, and the high concentration, the method of preparation from metallic sodium was not feasible. Repeated tests in this laboratory have shown that sodium hydroxide solution prepared in this way contains the merest trace of carbonate. In any case, the purity of the chemicals used hardly comes into question, since, in every case, the properties of the solution in which the optically active substance was subsequently dissolved, were determined. In no case were published figures relied upon. Nevertheless, in view of the intrinsic interest of all physical properties of sodium hydroxide solutions, it is worth pointing out that in every case where published figures are available, our own figures agree very closely.

#### Rochelle Salt.

The densities, refractive indices, and viscosities were all determined at 30.0°. The results obtained are given in Table I. The densities of solutions of Rochelle salt under the heading "calculated" were obtained by assuming that the dissolved Rochelle salt retained its density in the solid state (d = 1.767 for KNa  $C_4H_4O_6 \cdot 4H_2O_3$  hence, assuming, the water of crystallisation to have the density of ice, the density of anhydrous solid = r·7r). Hence the volume and weight of NaOH solution could be obtained. Thus the column headed "difference" corresponds to what is often called electrostriction and is therefore given the positive sign when the observed density is greater than the calculated. Solutions of Rochelle salt were always molar with respect to Rochelle salt. (210·19 gms. anhydrous Rochelle salt in I litre of solution.) The results are summarised in Table I.

It was not possible to carry the measurements beyond 12.15 N NaOH, owing to the increasing insolubility of Rochelle salt in NaOH. The heat effect chronicled under 14.5 N is therefore not a true heat of solution.

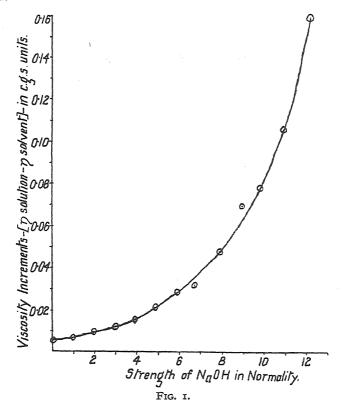
A critical scrutiny of the table yields the following conclusions: The density is not affected by increasing concentration of NaOH, as regards obedience to the mixture rule. There is always a small positive electrostriction. The variations in this quantity are irregular and are to be attributed, not to errors of experiment, but to the very rough value of "d calc." The most striking property is that of viscosity.

TABLE L--PHYSICAL PROPERTIES OF ROCHELLE SALT IN NAOH.

Heat of Solution.			* -1.152 K (anhydrous) -8.8 K	(hydrated) -0.895 K	-0.49 K	-0.455 K	-0.21 K	-0.25 K	-0.263 K	-0.215 K	-0.275 K	-0.14 K	-0.125 K	+0.187 K	+0.35 K	+1.25 K
	fer.	N <sub>F</sub> .	0.0290	.0252		.0205	8610.	0610.		.0173	.0153	.0134	9110.	0010.	.0104	
	Differ.	N <sub>C</sub> .	0.0285	.0246	.0232	.0206	1610.	8810.	7510.		.0159					)
Indices.	S.	N <sub>F</sub> .	1.3649	1.3727	1.380i	1.3874	1.3920	1.4005	1.4061	1.4086	1.4161	1.4220	1.4238	1.4274	1.4334	
Refractive Indices.	NaOH. + R.S.	N <sub>c</sub> .	1.3585	1.3661	1.3732	1.3808	1.3844	1.3931	1.3984	1.4004	1.4079	1.4135	1.4155	1.4172	1.4255	•
	NaOH.	N <sub>F</sub> .	1.3300 1.3359 1.3585 1.3649 0.0285 0.0290	1.3415 1.3475 1.3661 1.3727	1.3500 1.3561 1.3732 1.3801	1.3602 1.3669 1.3808 1.3874	1.3653 1.3722 1.3844 1.3920	1.3743 1.3815 1.3931 1.4005	1.3900	1.3837 1.3913 1.4004 1.4086	1.3998	1.4086	1.4038 1.4120 1.4155 1.4238	1.4165	1.4142 1.4230 1.4255 1.4334	
	Na(	$N_c$ .	1.3300	1.3415	1.3500	1.3602	1.3653	1.3743	1.3827	1.3837	1.3920	I.4004	1.4038	1.4086	1.4142	
Units.	Diff.		0.00534	.0065	2600.	6110.	or 21	.0210	.0285	.03168	.0475	.0695	.0780	1057	.1595	
Viscosity in c.g.s. Units.	NaOH + P S	Ç.W.	0.01335	.0162	.0210	.0273	.0344	.0465	.0618	6890.	0001.	.1460	.1646	7722.	.3042	
Viscos	NaOH.		10800.0	2600.	.01130	·0154	.0193	.0255	.0330	.0372	.0525	.0765	9980.	.1220	.1447	
	Diff.		+0.040	+ .045	+ .040	+ .034	610. +	+ .048	+ .042	+ .034	+ .034	+ .032	+ .025	+ .032	+ .038	
ity.	Calc.		1.087	1.115	1.155	1.190	1.230	1.235	1.270	1.290	1.325	1.360	1.430	1.460	1.480	
Density.	NaOH + R.S.		1.129	1.160	1.195	1.224	1.249	1.283	1.312	I.324	1.326	1.392	1.455	1.492	1.518	
	NaOH,		Î	1.038	1.078	1.120	1.151	1.187	1.213	1.237	1.270	1.317	1.388	1.428	1.455	
			•	•	•	•	•	•	•	•	•	•	•	•	•	•
Solvent.			Water $(d = 0.9957)$	o.97 N NaOH	1.94 N	3.03 N ",	3.92 IV ,,	4.90 IV ",	5.92 W ",	N 0/.0	, VI 00 //	. , N 56.0	. " N 08.6	, , , , , , , , , , , , , , , , , , ,	12:15 N ,,	14.5 W ".

\* From these figures the heat of hydration is calculated as + 7·65 large calories.

When the difference between viscosity of solvent and solution is plotted against concentration of sodium hydroxide, the following graph is obtained.



The figure also shows that the increment in viscosity produced by dissolving a constant weight of Rochelle salt is about thirty-two times as great in 12·15 N NaOH as it is in water, or about twenty-three times what it is for 0·97 N NaOH. This is strong evidence in favour of increasing association of NaKC<sub>4</sub>H<sub>4</sub>O<sub>6</sub> molecules with NaOH molecules.

The difference in refractive index produced by dissolving Rochelle salt shows a small but distinct decrease. Perhaps this might be taken to indicate that the "complex" is more than a mere loosely associated compound, and that a chemical rearrangement takes place.

Similarly with the heat of solution, there is a small but distinct change from a small negative to a small positive value.

#### The Isolation of the Complex.

A bold speculation, based on the phase-rule diagram  $^1$  might attribute to the tartaric acid-sodium hydroxide complex the formula  $C_4H_6O_6$ . 4NaOH, that is perhaps,

The solid phase obtained in these experiments was a gelatinous sticky mass, unlike either tartaric acid or sodium hydroxide.

Attempts were made to isolate the Rochelle salt complex as follows: Solid anhydrous Rochelle salt was warmed with 14.5 N NaOH and stirred vigorously. The undissolved salt was filtered off and the filtrate concentrated by warming under suction. On allowing to stand 24 hours, a voluminous gelatinous mass separated. This was filtered as dry as possible, by suction, and analysed for sodium hydroxide, by titration with acid, using phenolphthalein as indicator, and for Rochelle salt by precipitation as silver tartrate. The results yielded 34.8 per cent. NaOH; 52·1 per cent. Rochelle salt; or + 40·3 per cent. NaOH; 59·7 per cent. Rochelle salt on the dried specimen. The formula  $C_4H_4O_6NaK$ . 4NaOH requires 43 per cent. NaOH; 57 per cent. Rochelle salt.

In subsequent work, the samples were dried in a vacuum desiccator over sulphuric acid. A number of determinations of NaOH on separate preparations, yielded the following percentages of NaOH: 40.3 per cent.; 37.0 per cent.; 36.5 per cent.; 37.0 per cent.; 24.6 per cent.; 28.6 per cent. If the preparations contained complex they must also have contained excess free soda. Accordingly, a fresh preparation was washed with 95 per cent. alcohol, dried and analysed. This gave 21.3 per cent. NaOH. Finally a preparation was refluxed twice for several hours with 500 c.c. of 95 per cent. alcohol. This sample still contained 160 per cent. It is difficult to believe that mere adsorptions of sodium hydroxide on Rochelle salt is tenacious enough to resist this treatment with a solvent in which it is fairly soluble. On the whole, we think we are justified in saying that the complex has a sodium hydroxide content of between 20 and 40 per cent., i.e., that it contains either two, three or four molecules of NaOH per molecule of Rochelle salt.

If there existed a solvent immiscible with water, in which Rochelle salt were insoluble and NaOH slightly but distinctly soluble, it would be possible to investigate the formula of the complex by the distribution method. Attempts were made using ether, and investigating the NaOH in the ether layer by shaking with water and using a hydrogen electrode, but the results were too fluctuating to be used. Again, a mathematical treatment of the experimentally determined transport number should yield the formula of the complex, but experiment showed that in concentrated NaOH solution of Rochelle salt, the current is entirely carried by the ions of NaOH. We were, therefore, reluctantly obliged to leave the matter in this uncertain state.

Examination of a molar solution of Rochelle salt in Tyndall's beam showed the solution to be optically empty. Despite its high viscosity, therefore, the solution is not colloidal.

#### Mandelic Acid.

The properties of i-mandelic acid in molar solution, and of l-mandelic acid in decimolar solution, in sodium hydroxide, were investigated. The results for l-mandelic acid are contained in Table II.

As before, the differences between observed and calculated density can have no significance. With so small an amount of mandelic acid (0.76 gm.) the experimental error is large. For this reason also, somewhat large and irregular values of the heat of solution were obtained. When, however, the figures for viscosity are considered, we find the identical

TABLE II.—Physical Properties of l-Mandelic Acid in NaOH. 1/200 Mol. in 50 c.c. Solution.

Heat of Solution.*			- 2.8 K					-	Mean	value =	10.6 K						
	#	$N_{\mathrm{P}}$ .	0.0034	.0040		.0012	.0039	.0020	.0028	.0048	.0023	1			.0039	.0055	.0032
	Diff.	N <sub>c</sub> .	0.0032	.0041		8000.	.0020	.0047	6900.	.0044	.0026	.0032	.0025	.0028	.0040	.0105	.0029
e Indices.	+ M.A.	$N_{\mathrm{F}}$	1.3300 1.3359 1.3332 1.3393 0.0032 0.0034	1.3300 1.3359 1.3341 1.3399		1.3487	1.3600	1.3689	1.3780	1.3863	1.3923	1	1.4030	1.4111	1.4038 1.4120 1.4078 1.4159	1.4220	1.4262
Refractive Indices	NaOH + M.A.	$N_C$	1.3332	1.3341		1.3423	1.3520	1.3622	1.3711	1.3787	1.3853	1.3869	1.3945	1.4032	1.4078	1.4191	1.4171
	NaOH.	N <sub>F</sub> .	1.3359	1.3359		1.3415 1.3475 1.3423 1.3487	1.3500 1.3561 1.3520	1.3606 1.3669 1.3622 1.3689	1.3722	1.3743 1.3815 1.3787 1.3863	1.3827 1.3900 1.3853	1.3913	1.3920 1.3998 1.3945	1.4086	1.4120	1.4086 1.4165 1.4191 1.4220	1.4142 1.4230 1.4171 1.4262
	Na(	$N_c$ .	1.3300	1.3300		1.3415	1.3500	1.3606	1.3653	1.3743	1.3827	1.3837	1.3920	1.4004	1.4038	1.4086	1.4142
Jnits,	Diff		.000557	.00049		000040	.00059	91000.	·0004	+0000	.00049	.00122	.00175	.0032	.0123	.0213	1090
Viscosity in c.g.s. Units.	NaOH T	M.A.	795800.	.0085		1010.	68110.	.01551	.01937	.02589	.03349	.03844	.05425	2620.	6860.	.1433	.2048
Viscos	HOeN		10800.0	(O.H)		2600.	.01130	0.01535	.0193	.0255	.0330	.0372	.0525	.0765	•0866	.1220	.1447
	Diff		003	500. —		900.+	400	800.+	+ .042	+ .039	+ .045	+ .044	+ .025	920. +	+ .002	+ .021	600. +
ity.	J.		1.002	1.008		1.035	1.085	1.115	1.155	1.195	1.215	1.245	1.275	1.295	1.395	1.415	1.452
Density.	NaOH +	M.A.	0.9990	1.003		1.041	1.078	1.163	1.197	1.234	1.269	1.289	1.330	1.371	1.397	1.436	1.461
	NaOH		7566.	(O <sub>2</sub> H)		1.038	1.078	1.120	1.151	1.187	1.213	1.237	1.276	1.317	1.388	1.428	1.455
Solvent.				t ·97 N. to	neutralise acid	NaOH	•	•					•		•		•
Sol			Water	Sufficient ·97 N. NaOH to	neutra	0.97 N NaOH	1.94 N	3.03  N	3.92 N	4.90 N	5.92 N	6.70 N	7.88 N	8.95 N	9.80 N	N 06.01	12.15 N

\* From these figures the heat of neutralisation of l-mandelic acid by NaOH results as + 13.4 large calories.

behaviour, although less marked, to that of Rochelle salt in sodium hydrox-

\*:

A X OX

**XXXXXXX** 

From these figures the mean heat of neutralisation of i-mandelic acid by NaOH results as 12·1 large calories

ide, viz., the viscosity increments increase with increasing concentration of sodium hydroxide to about twelve times their original value, in 12·15 N NaOH. The refractive index differences are small and irregular, for the reason given above. Increasing insolubility prevented the measurements being carried beyond 12·15 N NaOH.

The figures for inactive mandelic acid (in molar solution) are contained in Table III.

The density differences are irregular, but it is somewhat striking that, as in the case of the lævo acid, there is a distinct change of sign at about 3 N NaOH. The variation in the heat of solution is presumably experimental error. The increase in viscosity increment with increasing concentration of sodium hydroxide is, however, very marked. There is also a marked progressive decrease in the refractive index increments, as in the case Rochelle salt in ofsodium hydroxide.

An attempt was made to determine the physical properties of mandelic acid in 11.24 N HCl, but the figures were vitiated by the escape ofhydrogen chloride from this strong acid which rendered the figures uncertain. Solutions in hydrochloric acid of lower concentration than this were of no interest, because it was previously found 4 that racemisation is not brought about, under the conditions of experi-

	Heat of Solution			- 2.4	0.6 +	8.5	10.3	6.4	2.6	10.5	10.1	10.1
N.)		<b>,</b> ,,,	$N_{\mathbf{F}^*}$	0.0252	2610.		.0300	6610.	.0187	+910.	1	antidana papanin di baga
Solutio		Diff,	N <sub>c</sub> .	0.0240	2810.					.0150	92000	
, c.c.	e Indices.	NaOH + M.A.	$N_{\mathrm{F}}.$	1.36.1	1.3672	1.3500 1.3561 1.3726 1.3798	1.3602 1.3669 1.3787 1.3869	1.3921	1.4002	1.4064	1	аОН.
L. IN 5	Refractive Indices.	NaOH	$N_C$	1.3540	1.3602	1.3726	1.3787	1.3854	1.3921	1.3977	1.4023	on of N
( Po MC		NaOH.	N <sub>F</sub> .	1.3359	1.3475	1.3561	1.3669	1.3722	1.3815	1.3900	1.3837 1.3913 1.4023	entratio
аОН.		Na(	$N_c$ .	1.3300	00291 1.3415 1.3475 1.3602 1.3672	1.3500	1.3602	1.3653	1.3743	1.3827	1.3837	is conc
CID IN N	Units,	2	Diff.	0.00274	16200.	.00432			.00717   1.3743   1.3815   1.3921   1.4002		0110	Not soluble in this concentration of NaOH
NDELIC A	Viscosity in c.g.s. Units.	NaOH	ж. Ж.А.	0.01075 0.00274 1.3300 1.359 1.3540 1.3611 0.0240 0.0252	.01261	.01562	.01973	.02477	.03267	.04160	.04820	Not so
s of i-Ma	Viscos		NaOH.	10800.0	2600.	.01130	.01535	.0193	.0255	.0330	.0372	ò
ROPERTIES		1	ii.	-0.015	210	010. —	710		+ .056	•		
SICAL P	ity.		Calc.	1.040		1.102	1.147	1.162	I.182	I.232	1.252	,
.—Рну	Density.	NaOH	M.A.	1.025	1.055	1.092	1.130	1.205	1.238	1.271	1.285	)
TABLE III.—Physical Properties of $i ext{-Mandelic}$ Acid in NaOH. ( $rac{r^2_0}{2^0}$ Mol. in 50 c.c. Solution.)			маОн.	0.0057	1.038	1.078	1.120	1.151	1.187	1.213	1.237	5
T	Solvent.			Pure Water .	o.97 N (exact neutralisation)	I.94 N	3.03 N	3.92 N	4.90 N · ·	5.92 N	6·70 N	7.88 N

<sup>4</sup> J.A.C.S., 54, 4583, 1932.

ment, by hydrochloric acid of lower concentration than  $11\cdot 24$  N. Complex formation would not therefore be appreciable.

#### Discussion.

A review of the evidence contained in this and previous papers leaves little doubt of the existence of complex formation when Rochelle salt is dissolved in strong sodium hydroxide solution. In the case of mandelic acid, the viscosity figures given in this paper may also be taken to indicate the same thing. Nevertheless, the evidence in favour of complex formation in the case of mandelic acid is much less convincing. If, however, the theory that catalytic racemisation is preceded by complex formations is to obtain general validity it would seem that there must be complex formation between mandelic acid (or rather, sodium mandelate) and sodium hydroxide. This difficulty can easily be overcome by assuming that in the case of mandelic acid, in the cold or static condition, the proportion of complex formed is small, *i.e.*, that the equilibrium:—

mandelic acid + NaOH ⇒ Complex, is well over to the left-hand side.

This assumption is by no means in conflict with the fact, observed by us, that, under comparable conditions the velocity of racemisation of mandelic acid by sodium hydroxide is much greater than that of Rochelle salt. One has only to recall that in the intermediate compound theory of catalysis, the intermediate compound is required to possess a very restricted region of stability, it must be neither too stable nor too unstable. It appears, therefore, that the factor determining the efficiency of catalytic racemisation, like any other homogeneous catalysis, is the degree of instability of the complex and not its amount. From this point of view, catalytic racemisation is brought under the general head of homogeneous catalysis, and possesses no distinguishing feature.

#### Summary.

The densities, viscosities, refractive indices and heat of solution of Rochelle salt and of mandelic acid in a range of concentrated solutions of sodium hydroxide have been determined. The densities, viscosities and refractive indices of the sodium hydroxide solution used as solvents have also been determined.

It is shown that complex formation in the Rochelle salt solution is extremely probable and attempts to isolate the complex and assign its formula have been partially successful.

In the case of mandelic acid also some evidence of complex formation, resting on viscosity measurements, is adduced.

A general theory is proposed which brings catalytic racemisation under the head of homogeneous catalysis without distinguishing feature.

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# THE CORRECTION FOR THERMO-MOLECULAR FLOW.

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A mass of gas enclosed in two vessels, A and B, which are connected by a tube, will reach an equilibrium state such that the pressure everywhere inside is the same, providing that the temperature is constant over the whole apparatus. At high pressures, even if one of the vessels, A, is heated, this is still true, and, as is well known, Gay-Lussac's Law is obeyed. Below a certain critical pressure, depending on the nature of the gas and the dimensions of the apparatus in the region of the temperature gradient, it is found that the equilibrium pressure is always higher in the warmer vessel as long as the temperature difference is maintained, and moreover, the pressure is no longer proportional to the absolute temperature. This phenomenon was first observed by Neumann 1 and later by Feddersen.2 Both of these workers attributed it to the adsorption of gas in larger quantities at the lower temperature. Reynolds,<sup>3</sup> however, showed it to be in accordance with the Kinetic Theory and proved experimentally in an investigation with plugs of plaster of Paris and of meerschaum, at low pressures, that the equilibrium pressures on the two sides are connected by the equation:—

$$\frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}} \quad . \qquad . \qquad . \qquad . \qquad (1)$$

where  $T_1$  and  $T_2$  are the absolute temperature of the faces of the plug, and  $p_1$  and  $p_2$  are the corresponding equilibrium pressures.

Maxwell 4 has treated the case of a tube, with a uniform temperature gradient along its length and no porous plug, and has deduced an expression, solely from kinetic considerations, for the pressure gradient dp/dTfor gases at pressures, where the mean free path of the molecules is of the same order as the diameter of the tube. This was lost sight of until Knudsen <sup>5</sup> began his investigations. His treatment is clearer and more exhaustive than that of Maxwell, but their final equations agree except in the constant terms.

Knudsen assumes that the pressure at any point in the gas is given by the expression,  $p = \pi N m v^2 / 8$ , where account is taken of the Maxwell distribution of velocities, N being the number of molecules in unit volume, m the mass of the molecules, and v the mean velocity. Equilibrium here is not established by equalisation of pressure, but from the equality of the number of molecules which cross any unit cross-section, normal to the temperature gradient, in one second from either side. This is assumed to be  $\frac{1}{4}Nmv$ , from Meyer's equation for the number of molecules in a

<sup>&</sup>lt;sup>1</sup> Ber. D. Konigl. Sachs. Gesellsch. d. Wissensch. Mathem. Phys. Kl., 24, 49 ff.,

<sup>1872.
&</sup>lt;sup>2</sup> Pogg. Ann., 148, 302, 1873. <sup>3</sup> Phil. Trans., p. 127, 1879. 4 Ibid., p. 231, 1879.

gas at rest which strike unit area. It is apparent that the application of Meyer's equation is only permissible when the number of collisions in the gaseous phase is small compared with the number at the walls, i.e., at low pressures, where the mean free path of the molecules,  $\lambda$ , is large in comparison with the diameter of the tube, D. In order that these two conditions should be obeyed simultaneously in a uniform tube with a temperature gradient, the equilibrium pressures must be proportional to the square root of the absolute temperature, and therefore the equation of Reynolds is valid only when the mean free path is much larger than the diameter of the tube.

Knudsen <sup>5</sup> has shown that the phenomenon can be adequately explained by two opposing flows in the gas mass—an axial one, from the hotter to the colder region, and a surface flow along the walls in the reverse direction. At equilibrium, these are equal in magnitude. He assumes that any plane surface consists of toothlike projections of molecular dimensions, so that any molecule striking the walls is repelled in a direction, which is totally independent of the angle of incidence and, after reflection, obeys the Lambert Cosine Rule for the reflection of light from a glowing body. In consequence, any unit area of surface will receive a larger momentum from the collision of molecules coming from the warmer side, and therefore a tangential force along the walls is set up, tending to drive the molecules near the surface from the colder to the hotter parts. The axial flow is the ordinary passage of gas from a region of higher temperature to that of a lower one.

This "double streaming" must exist at all pressures, but can only be of importance at low pressures, where Poisseuille's Law is no longer valid. At higher pressures, the flows will be limited by the frequency of collisions in the gas phase and therefore the thickness of the surface layer can never be greater than that of the order of the mean free path of molecules. Consequently, as the pressure is increased the axial current becomes the main factor and then Gay-Lussac's Law will operate and

there will be equality of pressure throughout the apparatus.

The intermediate transition region between the two limiting cases is one of great difficulty from a theoretical point of view. Here, molecules come from points far enough away from the walls to have speeds which bear no relation to the temperature of the surface at the point of impact, and therefore the isothermal surface in the gas will not be perpendicular to the length of the tube and will become more oblique as the pressure is increased. Knudsen therefore has introduced a coefficient which slowly varies from zero (in the region where the Reynolds expression is true) to a constant value  $\frac{4}{3}$ , at pressures where the ordinary gas law is obeyed.

The critical pressures, defining this transition region, will depend chiefly on the magnitude of the ratio  $\lambda/D$  and moreover, the swiftness of the change will likewise depend on the radius of the tube and the nature of the gas used. The magnitude of the effect is a function of the temperature difference between the vessels, A and B.

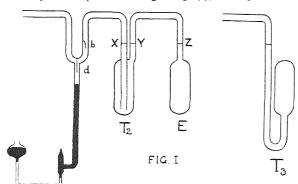
The object of this paper is to stress the magnitude of the Knudsen effect and in the case of fairly wide tubing, to emphasise the rapidity with which it varies with pressure. The results show that it is important to perform extensive calibrations, in order to obtain accuracy in the measurement of pressures, in any type of apparatus, wherein exists discontinuities of temperature, such as the presence of liquid-air traps, or furnaces, or in thermostatic work. Such corrections seem to have

been neglected except in the work of Langmuir 6 and Bawn.7 Both used hydrogen and the former gives as the limiting pressures between which the effect occurs, .0004 cm. and .004 cm. mercury, but mentions no dimensions. The latter did not reach the lower limit but gives or cm. mercury as the upper one in the case of 2 cm. tubing. Knudsen 5 has found, using a series of ten temperature junctions with capillary 0.374 mm. in diameter and a temperature difference of 500° C., that, at an equilibrium pressure of ½ mm. mercury, in the case of hydrogen, the pressure on the warm side was as much as ten times that on the cold.

We have shown later that, with a liquid air trap cooled to - 183° C., using hydrogen at 1  $\times$  10  $^{-3}$  cm. and tubing of 1 cm. diameter, the pressure inside is nearly 20 per cent. lower than that prevailing in the rest of the apparatus at room temperature. Such differences, in our case, decreased rapidly with increasing pressure until at  $1.4 \times 10^{-2}$  cm. the pressures were the same. With capillary tubing, however, the transition between the two limits is much slower and Knudsen has found differences to be apparent at pressures ranging from .001 cm. up to 60 cm., in his apparatus cited above. In the following pages are given the results of calibrations made on an apparatus used for studying adsorption at low temperatures and pressures.

#### Experimental.

The apparatus employed in this work was essentially the same as that used by Bawn (loc. cit., diagram p. 73), and given in Fig. 1 here but with-



the second out " blank " system. It consisted of a system containing calibrated gas burette, two McLeod gauges and mercury a U-seal leading to a trap,  $T_2$ , and a bulb, E. The mercury seal had pointers, b and d, fused into glass so that the level of the mercury could be ad-

justed to a definite mark each time, either when opened or closed. All glass connections were of 1 cm. tubing internal diameter. The volumes of the trap and the bulb, each to a definite level, were determined by means of mercury before erection. The total volume of the apparatus, with the mercury in the seal at d, and the volume of the McLeod system, with the level in the seal at b, were determined by allowing a known quantity of hydrogen from the gas-burette into the systems, measuring the pressure on the gauges and applying Boyle's Law. Pressures from  $I \times 10^{-3}$  to  $I \times 10^{-1}$  cm. mercury could be measured accurately on the McLeod gauges, which had been previously calibrated.

Hydrogen was used throughout, since, as in the work of Langmuir and of Bawn, it was found that no measurable adsorption on glass, either at room temperatures, or at 90° A. occurred. A further advantage is that this gas has the highest mean free path, so that extremely low pressures

could be avoided. It was prepared from pure zinc and hydrochloric acid, preliminarily purified by Dumas' method, and then allowed to diffuse through a palladium tube maintained at 300° C. and finally dried by passage through phosphorus pentoxide. On analysis, it was found to be 99.9 per cent. pure.

#### Method of Experiment.

In every measurement of pressure, three readings were taken with the mercury thread at various heights in the closed capillary of the gauge, and the mean of these taken. This avoided any errors due to the variation in the height of the meniscus, which occur despite the rigorous cleaning of the glass and the mercury, and also those due to a small, but varying, amount of the gas which is enclosed between the mercury and the glass walls. This latter depends on the height of the mercury thread in the gauge and on the rate of flow of the mercury up the McLeod. The speed of entry was kept constant by using an all-glass connection from the reservoir to the gauge, and operating it either by exhausting the former, or by connecting it to the atmosphere through a fine capillary. With this procedure, pressures agreed to within 0.2 per cent. generally.

Since the pressure difference, resulting from the thermomolecular flow, depends on the dimensions of the tube at the temperature junction, it was of the greatest importance to construct, not only the exit Y and the inlet X tube of the same internal diameter, but also that of the tube Z leading to the bulb E. If this is not observed, then the pressure above X will bear no relation to that above Y and Z, nor will the pressure in the bulb be the same as that in the trap. Experiments were tried with the bulb of the trap not completely enclosed in the cold bath, in order to estimate the error involved using different diameter of exit and inlet tubing, but the pressure measurements were very erratic and depended too largely on the accuracy of adjustment of the level of the bath to be of any value.

Before the expansion of the gas into the cooled vessels, it was necessary to put the liquid air around at least two hours previously, in order to obtain reproducible results within three to four minutes. On cooling after the admission of the gas, the equilibrium was not attained until thirty to forty minutes, depending on the quantity admitted. At first, liquid air was employed but the variation of the temperature caused fluctuations in the pressure, since the thermomolecular flow is very sensitive to temperature change in this region; this led to its being replaced by liquid oxygen.

The method of procedure was always the same. The whole system was evacuated to a pressure less than  $1 \times 10^{-6}$  cm. by means of a glass mercury diffusion pump, backed by a Hyvac oil pump. With the mercury seal at b, a quantity of gas was admitted and the pressures recorded as above. The seal was then dropped to d and the pressure measured after three minutes. This was repeated over a range of pressures ranging from  $1 \times 10^{-2}$  cm. to  $1.4 \times 10^{-2}$  cm., in each case completely exhausting before the introduction of a fresh quantity of gas, thus avoiding the cumulative error of adding successive small amounts. The second method employed—that of cooling the trap after admission of the gas—gave results in good agreement with those obtained above, if the equilibrium pressure was recorded 30 to 40 minutes after putting the gas in.

#### Results.

A typical series of results, in the case where the trap is cooled to 90° A., is shown in Table I.

The pressure in the McLeod system with the bulb and trap cut off by the U-seal, was measured. The volume of this,  $V_1$ , and that of the total system,  $V_2$ —with the seal open—are known, hence the pressure  $P_1$ , which

the gas would exert after expansion, when the whole apparatus was at room temperature, could be found from Boyle's Law. In consequence of the thermomolecular flow which occurred on cooling of the trap, the actual pressure now recorded on the gauge,  $P_2$ , will be smaller than  $P_1$ , and will represent the pressure which the gas exerts at all parts where the temperature is the same as that of the gauge. This volume,  $V_3$ , equals the total volume, minus that volume of the trap enclosed in the liquid oxygen  $(V_1)$ . Therefore, if  $P_L$  is the pressure of the gas in the cooled trap at 90°A., then

$$\frac{P_1 V_1}{T_R} = \frac{P_2 V_3}{T_R} + \frac{P_L V_L}{T_L},$$

where  $T_{\mathbf{L}}$  is room temperature and  $T_{\mathbf{L}}$  that of the liquid oxygen.  $P_{\mathbf{L}}$  can now be evaluated.

 $R_1$  is the ratio  $P_1/P_2$ ; this is plotted against  $P_2$  and the values of the former read off at definite intervals of pressure, and these taken for the

TABLE I.—Temperature of the Cold Bath,  $R_{\rm L}=P_{\rm L}/P_{\rm 2}$ , is the ratio of the pressure above X and Y

$P_2 \times 10^3$ cm.	R <sub>L</sub> (One Trap).	$R_{ m L}'$ (Two Traps).
ī	0.716	0.722
2	0.817	0.817
3	0.884	0.884
4	0.929	0.927
4 5 6	0.960	0.951
6	0.985	0.972
7 8	1.004	0.994
8	1.019	1.005
9	1.028	1.019
10	1.033	1.025
12	1.034	1.030
14	1.034	1.034
	1	1

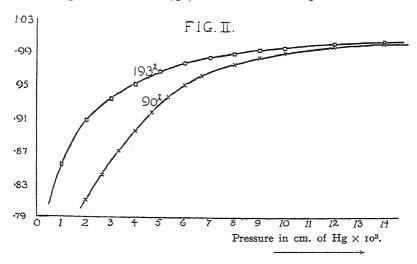
calculation of  $P_{\rm L}$  and  $R_{\rm L}$ .  $R_{\rm L} = P_{\rm L}/P_{\rm 2}$ , is the ratio of the pressure above X and Y to that in the trap.  $R_{\rm L}'$  is the ratio observed in the case where both the trap  $T_{\rm 2}$  and the bulb E are cooled. Providing the diameters of the connecting tubing are the same throughout,  $R_{\rm L}$  should be equal to  $R_{\rm L}'$ .

Two sets of apparatus were used. In Table I. are given the values obtained with apparatus I for  $R_{\rm L}$  and  $R_{\rm L}'$  at 90° A. The agreement is of the order of 1 per cent. If the volume of the part cooled had been a larger proportion of the

whole, then a greater accuracy would have been obtained. The measurement of pressures below 1 × 10-3 cm. was not sufficiently accurate, so that no attempt was made to reach the lower limit for the thermo-molecular flow. The upper limit found here was at 1.034 at a pressure of about  $1.4 \times 10^{-2}$  cm., but it is not very sharply defined. This value should, of course, be unity. The deviation from the theoretical value is probably due to the fact that in the calculation of PL, we have assumed that the temperature junction is ideally sharp, whereas the level of the bath was kept at a distance of about 4 cm. from the lip of the Dewar vessel and the top lagged with cotton wool. Consequently, there was an appreciable volume of tubing at a temperature of approximately - 110° C. within, in addition to a temperature gradient outside the Dewar. This causes all the values of PL to be high. One of us, using an entirely independent apparatus (apparatus 2) but identical in design, has obtained, by keeping the level almost flush with the lip of the Dewar, a magnitude of 1.002 for his limit. The plot of  $P_{\rm L}/P_{\rm z}$  for the second apparatus is shown in Fig. 2 for 193° A. and 90° A. (one trap only used).

Table II. shows the results obtained at 193° A. in apparatus 2 (solid carbon dioxide and alcohol),  $R_{00_2}$  being the ratio of the pressure of the gas outside to that inside the trap as above, when trap  $T_2$  only is cooled.  $R'_{00_2}$  is the ratio for a trap of the type  $T_3$ . Both types of trap give the same values within 0.5 per cent., showing that, as long as the tubing leading to the trap has the same internal diameter, then the magnitude

of the Knudsen effect is quite independent of the shape, or size, of the vessel. A plot obtained for 193° A. is also drawn in Fig. 2.



It will be noticed that the curve for 193° A. is always above that obtained at 90° A., showing that the magnitude of the effect is a function of

the temperature difference at the junction, and that the curves approach a constant value at the upper limit at approximately the same pressure. The lower limit here should be 0.813 so that the curve must straighten out very quickly as the pressure decreases and finally become horizontal.

#### Summary and Discussion.

The importance of an extensive calibration in any apparatus, containing parts at different temperatures has been illustrated, in the case of hydrogen at pressures

TABLE II.—Temperature of the Cold Bath, 193° A. Apparatus II.

$R_{\mathrm{CO_2}}(T_2)$ .	$R'_{\mathrm{CO}_2}(T_3).$
0.854	0·840 0·904
0.933	0.936
0.951	0·953 0·964
0.977	0.972
	0·979 0·985
0.993	0·989 0·992
1.001	0.999
1.004	1.002
	0·854 0·907 0·933 0·951 0·967 0·977 0·983 0·988 0·993 0·996

baths at 90° A. and  $193^\circ$  A., with tubing of 1 cm. at the temperature baths at 90° A. and  $193^\circ$  A., with tubing of 1 cm. at the temperature junction. In adsorption work at low pressures, where it is required to know, not only the equilibrium pressure of the gas in contact with the adsorbent, which is at a different temperature from that of the manometer, but also the amount of gas adsorbed, the correction may be as much as 20 to 30 per cent. for the pressure, and even where the volume cooled is small compared with the total volume, as in the apparatus described, the discrepancy may well lead to errors of the order of 5 per cent. in the amount of gas adsorbed. In consequence, the derivation, kinetically, of the heat of adsorption from isotherms at different temperatures, will give values which have no true meaning in an absolute

sense. In the same way, heats of activation of such processes, deduced from pressure/time curves, will require correction, since, for example, in low temperature work, the observed rates will be sensibly much quicker than the true ones, particularly so at the lower temperature; and vice versa at high temperatures. In the static determination of low vapour pressures, in the construction of diffusion pumps and in the use of gas thermometers, especially in the case of hydrogen, note must be taken of this phenomenon.

Such corrections are of importance not only at low pressures. They become essential as soon as the pressure of the gas is such that its mean free path approaches that of the diameter of the tube at the temperature junction. As observed previously, Knudsen has found an appreciable

effect with narrow capillary tubing even at 60 mm. of hydrogen.

The mode of construction of the traps is of importance. Unless the exit and inlet tubes are of the same diameter, an effective "pressure barrier" may be produced between different parts of the apparatus which will make it impossible to deduce the actual pressures in that part of the

apparatus beyond the trap.

Both Langmuir and Bawn have assumed that for other gases the ratio  $R_{\rm L}$  will be the same as that for hydrogen, at pressures at which the mean free paths are equal. Experimental verification at low pressures is complicated by the fact that most gases are adsorbed on glass at 90° A. and 193° A. With carbon monoxide and argon we could find no appreciable adsorption on glass at  $1 \times 10^{-3}$  to  $1 \times 10^{-2}$  cm., and the ratios found for the Knudsen effect were in agreement with those calculated on the above hypothesis. Theoretically, this is not quite rigid, since viscosity factors and the frictional resistance to the surface flow along the glass will vary with the gas. These, however, must be small.

A further point of interest is the time of attainment of pressure equilibrium when the bulb is filled with a powdered substance. This was found to be about ninety minutes. Knudsen, with a plug of magnesia, has found a slow creep even after forty-eight hours. This may be an important factor in the slow diffusion, or solution, characteristic of

'secondary'' adsorption processes.

The authors wish to express their appreciation to Professor W. E. Garner for his interest in the work. One of us (D. E. W.) wishes to express his indebtedness to Imperial Chemical Industries Limited for a grant towards the cost of apparatus and to Messrs. Nobel's Ltd. for a personal grant, and the other F. C. T.) to the Department of Scientific and Industrial Research for a personal grant.

Department of Physical Chemistry, The University, Bristol.

8 Loc. cit., p. 633.

# AN INTENSITY FILTER FOR THE MERCURY LINE AT 253.7 m $\mu$ .

By H. W. Melville and H. J. Walls.

Received 12th September, 1933.

In photochemical chain reactions, the effect of the variation of the intensity of the incident radiation provides important information about the termination of the chains. If the rate of reaction is proportional to the first power of the intensity, it may be concluded that the chain carrier is destroyed in a bimolecular collision with another molecule or by a collision with the walls of the reaction tube. On the other hand, if the rate is proportional to the square root of the intensity, the chains are terminated by self-destruction, e.g., by the combination of two atoms. Examples of these types of behaviour may be seen in the recent series of papers on the hydrogen-chlorine reaction by Ritchie and Norrish.1 This differentiation in the mechanism of chain termination has now gained added importance, for it is believed that the position of the upper and the lower limits for explosion of thermal chain reactions is determined respectively by gas phase and by wall destruction of the carriers. Photochemical experiments on the intensity relationships outside these limits should be able, therefore, to give confirmation of the hypotheses which have been advanced to explain these phenomena.

No great difficulty occurs in measuring the variation in intensity when a thermopile or photoelectric cell is employed and the reaction vessel is at room temperature. If, however, the reaction bulb is in a furnace and the source of light is of considerable area, such as a mercury lamp, the difficulties are increased. Some means are, therefore, required to vary the intensity by a known and easily controllable amount. The rotating sector is not suitable for this type of work, as it really alters the duration of exposure and not the intensity.<sup>2</sup> In addition, matters are rendered more complicated by the possible existence of induction periods and photochemical after effects. Wire gauze screens, especially if constructed of round wire, are not, in general, reliable as it is difficult to calculate exactly how much light is cut off. There remains then some type of filter partly transparent to the radiation being used.

This paper is concerned with a liquid filter for use with the mercury resonance line at 253.7 m $\mu$  and hence is specially suitable for mercury sensitised reactions. In order to vary the transmission of a liquid filter, a solution is most convenient to use as only a single cell is required. The solution must, however, have the following properties if it is to be reliable (a) stability to light of 253.7 m $\mu$ , (b) components to be easily obtained in a pure state, (c) normal behaviour of the components so that Beer's law is obeyed exactly, (d) rapidity and ease of preparation.

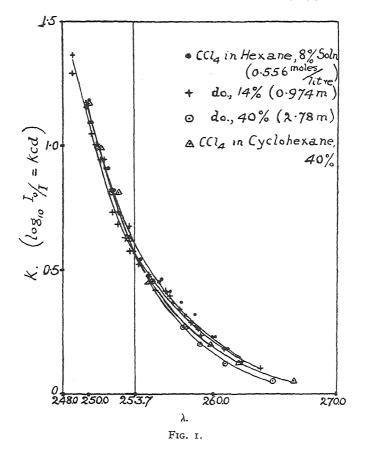
These criteria are fulfilled by mixtures of carbon tetrachloride and n-hexane or cyclo-hexane. Ordinary sulphur free carbon tetrachloride is suitable, but the hexane or cyclo-hexane must be specially purified

<sup>&</sup>lt;sup>1</sup> Proc. Roy. Soc., 140A, 99, 112, 713, 1933. <sup>2</sup> Griffith and McKeown, Photochemical Processes, p. 664.

in order that its absorption at 253.7 m $\mu$  may be negligible. The n-hexane and cyclo-hexane purified for spectroscopic work, as supplied by British Drug Houses, were used in the present instance and found to be entirely satisfactory. The rapid rise in the extinction coefficient of carbon tetra-chloride to light of 253.7 m $\mu$  cuts out all light from the mercury arc which might be absorbed by the reactants directly. One advantage of using cyclo-hexane in preference to n-hexane is that its boiling-point is close to that of carbon tetrachloride and therefore any loss of the solution by evaporation, e.g., when placed in the proximity of a furnace, does not lead to any disturbing change in concentration.

## Experimental.

A 5 mm. absorption cell was employed for the photochemical experiments. A series of solutions was therefore made up to cut off from 20 percent. to 80 per cent. of the light as measured approximately by the photochemical reaction. The extinction coefficients of the solutions were then



measured exactly by means of a Bellingham and Stanley rotating sector photometer used in conjunction with a Bellingham and Stanley quartz spectrograph, giving the spectrum from about 210 to 800 m $\mu$  on a 10 in. plate. An iron spark was employed as source of light. The wave-lengths

for the positions of equal blackening on the plate were determined by comparison with an enlarged calibrated photograph of the iron spark spectrum, the plates being examined with the aid of a lens. The positions were determined at least twice in each plate, with an interval in between, in order to eliminate possible errors due to fatigue. The wave-lengths could easily be determined to within  $o \cdot 2 \, \text{m} \mu$  in this way.

The extinction coefficient — wave-length curves for four solutions are shown in Fig. 1. The value of the extinction coefficient used is defined by the equation

$$\log_{10} I_0/I = kcd . . . (1)$$

where k is the extinction coefficient, d the thickness of the layer in cm., and c the concentration in moles per litre. It will be seen that the curves for three different concentrations (0.56, 0.97, 2.78 moles per litre) fall practically together; the difference in the ordinates may be put down to experimental error. This means that Beer's law is obeyed exactly within this region of concentration. The two solutions of equal concentration in hexane and in cyclohexane also show identical absorption in this region.

The values of k at 253.7 m $\mu$  as measured off a large scale graph are:—

Using this value of k, the percentage transmission for any concentration and layer thickness, or alternatively the concentration and/or layer thickness necessary to cut off a given amount of radiation at 253.7 m $\mu$ , can be rapidly calculated by means of equation 1.

To test the stability of the filter, a solution of concentration 2.78 moles per litre made up with hexane was exposed to a mercury lamp with a cool cathode running at 5 amps. and 40 volts for four hours. Some change occurred, for the liquid evolved some hydrochloric acid and it was found that the extinction coefficient at 253.7 m $\mu$  had increased by about 20 per cent. A similar result was obtained with cyclohexane. A filter was therefore not employed for much longer than fifteen minutes. As the quantity of solution required to fill the quartz cell only amounted to a few c.c., this procedure was not unduly extravagant in the use of the comparatively expensive hexane.

In the Tables below are given data of a few experiments on the mercury sensitised reaction between hydrogen and nitrous oxide. The investigation 3 of the thermal reaction had shown that it was of the chain type,

TABLE I.—Low Press. 5 cm. Reaction Bulb. Temp. 580° C. 1:1 Mixture. Total Press. 16.00 mm.

Composition of Filter.		Rate Rel. to Hexane (R).	Intensity Rel. to Hexane (I).	R/I.	
n-hexane			1.00	1.00	1.00
1.2 c.c. in	25 C.C.	solution	o·86	0.80	1.07
2.0 ,,	,,	,,	0.70	0.68	1.03
2.0 ,,	,,	,,	0.73	0.68	1.07
3.5 ,,	,,	,,	0.53	0.51	1.04
10.0 ,,	,,	,,	0.183	0.15	1.20

The absolute rate of reaction with pure hexane was 0.82 mm. of water per min.

<sup>&</sup>lt;sup>3</sup> Melville, Proc. Roy. Soc., in the press.

Composition of Filter.	Rate Rel. to Hexane (R).	Intensity Rel. to Hexane (I).	R/I.	R <sup>2</sup> /I.
n-hexane	1·00	1.00	1·00	1.00
	0·80	0.68	1·17	0.94
	0·67	0.51	1·31	0.87
	0·49	0.38	1·29	0.64

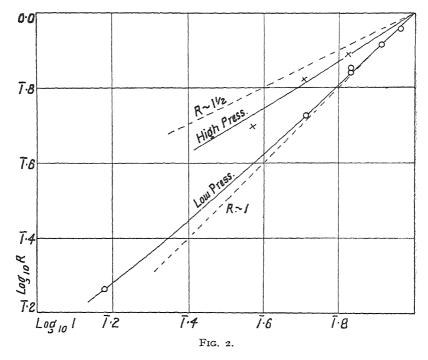
TABLE II.—High Press. Temp. 510° C. 1:1 Mixture. Press., 100 mm.

The absolute rate of reaction with pure hexane was 0.80 mm. water per min.

initiated by the dissociation of a nitrous molecule into  $N_2$  and O, followed by the reaction  $O+H_2\to OH+H$ . The chain is probably propagated by the reactions

$$\begin{array}{l} \mathrm{OH} + \mathrm{H_2} \! \rightarrow \! \mathrm{H_2O} + \mathrm{H} \\ \mathrm{H} + \mathrm{N_2O} \! \rightarrow \! \mathrm{OH} + \mathrm{N_2}. \end{array}$$

Further, there was indirect evidence that the chains were terminated principally in the gas phase by self-neutralisation at pressures of the order of 100 mm., whereas at 10 mm., wall deactivation was most important. It would be expected then that in the photochemical experiments, (a) at



high pressures the rate should be proportional to the square root of the intensity, and (b) at low pressures, a linear relation should hold between rate and intensity.

Full details are not given of the experiments (they will be published later) as the results quoted are solely for the purpose of indicating the

usefulness of the filter in providing independent confirmation of the mechanism of the termination of the chains.

In Table I., it will be observed that the rate (R) is very nearly proportional to the intensity (I) as is indicated by the constancy of the quantity R/I. At high pressures R/I is no longer constant and neither is  $R^2/I$  so that the rate must be proportional to a power of the intensity between 0.5 and 1.0. Even at 100 mm., however, wall termination was quite noticeable and the latter result is to be expected. The dark reactions were negligible in both cases; the chain length was of the order  $10^2$ .

In Fig. 2,  $\log_{10} R$  has been plotted against  $\log_{10} I$  using the results in Tables I. and II., and it will be observed that the high pressure experiments lie fairly close to a line having a slope of 0.5, whereas the low pressure experiments conform nearly to a line of unit slope.

#### Summary.

A liquid filter is described for altering the intensity of the 253.7 m $\mu$  line from a mercury arc lamp. The absorbing liquid is sulphur free carbon tetrachloride which is mixed with n-hexane or cyclohexane. The extinction coefficients of a number of solutions were determined and found to obey Beer's law. The applicability of the filter is shown by experiments on the photochemical chain reaction between hydrogen and nitrous oxide at high and at low pressures where the rate is respectively proportional to the square root and to the first power of the intensity.

The authors are indebted to the Carnegie Trustees for the award of two scholarships.

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#### REVIEWS OF BOOKS.

Von Davy und Döbereiner bis Deacon, ein halbes Jahrhundert Grenzflächenkatalyse. By A. MITTASCH and E. THEIS. (Berlin: Verlag Chemie, G.m.b.H., 1932. Pp. 278 with 16 plates. Price bound 18.50 marks.)

The authors, chemists of the I.G. Farbenindustrie, have had the opportunity of consulting much of the earlier literature on contact catalysis and had the happy thought of making the stores of knowledge thus gained available to other chemists. Their book, which is very ably written and produced, covers a fruitful period in the development of the subject with which it deals, and in addition to being an important contribution to the history of chemistry and chemical industry, it contains a great number of facts of present importance and value. To the specialist in the history of chemistry it will in some respects be disappointing, since although original sources have obviously been principally used, these are not infrequently quoted with errors in the text and even sometimes in the references, as when the paper by Kuhlmann on the oxidation of ammonia is said to be in Liebig's *Annalen*, whilst in actual fact it is in the *Annales de Chimie et de Pharmacie*. The short biographical notes in the text and footnotes are also marred by errors, and names are incorrectly given, apparently because too much reliance has been placed in memory. These features will not disturb the general reader, and the book as a

whole will be found interesting. It gives in a reasonable space a clear and authoritative account of its subject. The bearings of much of the older work on modern theories and processes are pointed out and this and other features, including the excellent tables summarising the topics dealt with, make the book of much more than historical interest. The authors deserve our thanks for the great amount of work which its preparation has involved, and should receive our congratulations on such a successful conclusion to their labours as the present book. It can be recommended to chemists as a book worth possessing and reading.

J. R. P.

Rechenverfahren und Rechenhilfsmittel mit Anwendung auf die analytische Chemie. (Die Chemische Analyse, Band xxx.) By Professor Dr. Otto Liesche. (Stuttgart: Ferdinand Enke, 1932. Pp. viii + 201. Price, paper covers 20 R.M.; bound 22 R.M.)

Professor Liesche's book covers the whole ground of methods of calculation, with special reference to analytical work, in a very thorough manner. The short methods of arithmetical computation are dealt with, including Ferrol's methods of multiplication and division, which give results much more rapidly than the usual methods; logarithms; slide rules; calculating machines; algebraic formulæ; indirect analysis; errors; and nomography. In laboratories where much calculation is involved the book should prove very useful, and many of the methods described will certainly save the individual worker much time and labour.

The author has provided a good collection of examples to illustrate each section, and there is no doubt that anyone who uses the book in the way the author intends will become more expert in the performance of calculations, and that the methods described in it are worthy of study and trial. The section on the calculation of analyses of complex mixtures contains a good deal of information which is not otherwise easily available, and the book should be in the hands of all analytical chemists.

J. R. P.

Chemischer Handatlas. By W. WALTER MEISSNER. (Braunschweig, etc.: Verlag Georg Westermann, 1931. Pp. x + 77 and 60 charts in colours. Price 38 gold marks.)

This atlas, which is convenient in size and has the text and plates bound together, provides an excellent survey of the properties and characteristics of the chemical elements. The main interest is from the point of view of atomic structure but the field surveyed is really extensive, such matters as geographical distribution, geochemistry, separation, heats of formation and solubilities of compounds, etc., being included. The headings of the charts are in five languages, English included, although the text is in German only. There are author and subject indexes and numerous references to the literature in the text. This book is likely to prove very useful to chemists and physicists and may be recommended. Some errors not covered by the list on page 77 were noted.

I. R. P.

ABERDEEN: THE UNIVERSITY PRESS

# THE RATE OF DECAY OF HYDROGEN AND OXYGEN OVERVOLTAGES.

By G. Armstrong and J. A. V. Butler.

(Received 28th Fune, 1933.)

In the older theories of the hydrogen overvoltage it was often postulated that the phenomenon was due to an accumulation of atomic hydrogen at the electrode, which set up a back electromotive force. Gurney 1 has recently shown that the experimental relation between the current density i and the potential V, viz.,  $i = ke^{-aV}$ , can be accounted for as a result of the conditions of transfer of electrons from the electrode to hydrogen ions in the solution, and has suggested a way in which the experimental value, which is conveniently expressed as  $-\Delta V/\Delta \log_{10} i = 2.303/a = 0.120$  at 15°, 2 can be derived.

A very definite test of the activity of the product of the electrolysis is afforded by the study of the decay of the overvoltage at open circuit. If the products of the electrolysis have no appreciable electromotive activity (i.e., do not yield electrons to the metal at any appreciable rate), electrons should continue to pass from the electrode to the solution at a rate determined by the potential, according to the equation given above, when the current is stopped. Since there is no current through an external circuit, this transfer must cause a reduction of the charge of the double layer and consequently a fall of the potential difference of the electrode.

If the capacity of the double layer is B, the rate of change of the potential with time at open circuit is given by dV/dt = i/B, where i is the rate of transfer of electrons across the double layer. Introducing the value of i given above, we have  $dV/dt = ke^{-aV}/B$ , or  $e^{aV}$ . dV = (k/B). dt. Integrating this between the times o and t, and the corresponding potentials  $V_0$  and  $V_t$ , we obtain

$$(e^{aV_t} - e^{aV_0})/a = kt/B$$
,

and writing  $i_0 = ke^{-aV_0}$ , this becomes

$$e^{aV_t} = akt/B + k/i_0 = (k/i_0)[ai_0t/B + 1]$$
 . (1)

Since a/B is of the order of 107, and  $i_0$  is usually about 10  $^{-4}$ , the term 1 can be neglected for all except very small vaues of t. We then have

$$aV_t = \log_e(ka/B) + \log_e t, \qquad (2)$$

Proc. Roy. Soc., 134A, 137, 1931.
 Tafel, Z. physikal. Chem., 50, 641, 1905; Bowden, Proc. Roy. Soc., 126A, 107, 1929.

and by plotting  $V_t$  against  $\log_{10} t$  we should obtain, except for very short times, a straight line having the slope  $\Delta V/\Delta \log_{10} t = 2.303/a$ , which

has the experimental value 0.120 volts.

If there were any electromotively active material near the electrode which could give electrons to the metal at the rate i' (for the potential V) the rate of change of the potential would be dV/dt = (i - i')/B. As the potential falls at open circuit i diminishes, but i' which represents the rate of a reverse process must increase. Consequently if an electromotively active substance is formed in the electrolysis, although i' might be insignificant compared with i at the steady potential  $V_0$ , they might become comparable at a lower potential and the rate of decay would then be much less than that calculated above. The activity of a very minute amount of an active product, provided that its life were sufficiently long, might thus be detected.

Similar considerations apply to the oxygen overvoltage, for which a has been found to have the same value. We have investigated the rates of decay at open circuit of the hydrogen overvoltage at mercury and platinum electrodes, and of the oxygen overvoltage at platinum

electrodes, both in dilute sulphuric acid solutions.

#### Experimental.

The apparatus was similar to that used in a previous investigation.3 The potential of the experimental electrode was determined by means of a Lindemann electrometer, a mercurous sulphate electrode in sulphuric acid being used as the reference electrode. The capacity of the experimental electrode is so small that the rate of decay is greatly influenced by even minute leaks, and it is essential to have every part of the apparatus, through which a leak could occur, thoroughly insulated. The experimental electrode was permanently connected with the needle of the Lindemann by a carefully insulated wire. Connection with the polarising battery was made when required by contact with this wire. When the decay of the overvoltage was being observed contact was broken at this point and the experimental electrode was connected only by this wire to the Lindemann.

Bowden 4 observed marked discontinuities in the decay of hydrogen overvoltages which he attributed to minute traces of metallic impurities, which are not removed by the ordinary methods of purification. We used a good quality of conductivity water and sulphuric acid (As. T.) twice redistilled from pyrex apparatus and only the middle fraction collected. We did not coat the inside of the experimental vessel with wax as Bowden did, as it is almost impossible to prevent the solution coming into contact with glass at some stage. The vessels had been in use in similar experiments in dilute sulphuric acid for over a year, and it was thought that the more soluble parts would have already been removed.

The sulphuric acid was rigorously freed from oxygen by boiling at reduced pressure in a stream of purified hydrogen for a considerable time before introduction into the cell. The mercury was twice redistilled and was introduced into the cell after the latter had been filled with hydrogen.

Decay of the Hydrogen Overvoltage at Mercury and Platinum Electrodes. —When the initial potential of the electrode did not much exceed  $\epsilon_{\text{H}} = -$  1.0 volts, it was found the rate of decay was in good agreement with (2). Fig. 1 shows V plotted against  $\log_{10} t$  in a number of typical experiments. For times up to 1000 seconds a good linear relation is ob-

<sup>&</sup>lt;sup>3</sup> Proc. Roy. Soc., 137A, 604, 1932. 
<sup>4</sup> Trans. Faraday Soc., 23, 571, 1927.

tained and the slope,  $\Delta V/\Delta \log_{10} t = \text{o·}125$  is in good agreement with the calculated value. It is thus evident that over the range shown the theoretical curve has been realised, and above  $\epsilon_{\text{H}} = -\text{o·}35$  there is no sign of any electromotive activity by atomic or molecular hydrogen. After 1000 seconds the rate of change, which is then very small, varied somewhat eratically being sometimes greater and sometimes less than that calculated.

When the original potential of the electrode is considerably more negative than  $-1 \cdot 0$  volts, *i.e.*, with larger polarising currents, much slower

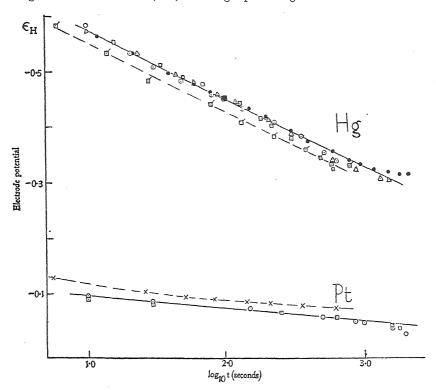


Fig. 1.—Decay of hydrogen overvoltages at mercury and platinum electrodes.

rates of decay are observed. Fig. 2 shows the decay curves obtained in successive experiments after polarisation with a current which raised the potential to  $\epsilon_{\rm H} = -$  r·55 volts. The rate of decay after successive polarisations steadily decreases, and the potential finally remains nearly constant at a high negative value. Bowden 4 attributed this persistence of the overvoltage to the deposition in the mercury of minute traces of metals. Our experiments also support this conclusion. That the high potential is due to material deposited in the mercury is shown by experiments (5) and (6). On shaking the apparatus sufficiently to cause some oscillation

of the mercury in the cup the potential rose considerably and when quiescent soon diminished again. The effect of shaking is thus to bring active material from the interior of the mercury to the surface. Attempts to eliminate the persistence of the overvoltage after polarisation with a high current density by careful purification of the solutions and also by electrolysing the stirred solution for many hours with an auxiliary mercury cathode were unsuccessful.

In order to estimate the quantity of active material deposited an electrode was polarised cathodically for a time with a large current and then a small anodic current was passed in order to remove the active material deposited. The greater part of the active material was removed in the first anodic polarisation, for although shaking the electrode when the

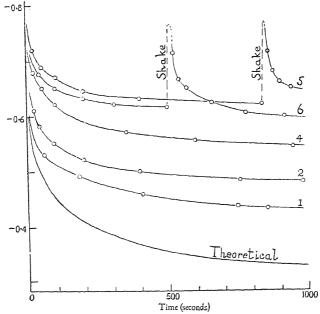


Fig. 2.—Decay of hydrogen overvoltage at mercury electrodes, after successive anodic polarisations with large current (2 cm. $^2$  electrode, polarising current 15.6  $\times$  10-3 amps).

Cathodic polarisation: 1, 2 and 3, 3 min.; 4, 10 mins.; 5, 20 mins. (not shown); 6, 3 mins.

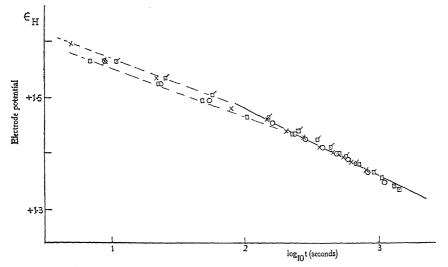
potential had reached - 0·3 caused it to rise again, the quantity of anodic polarisation required to bring it again to this value was comparatively small. Experiments were made with (1) a highly purified sulphuric acid solution, (2) the same solution to which a small quantity of sodium sulphate had been added, making it 10  $^{-4}$  N with respect to sodium ions. The anodic break observed in both cases was near  $\epsilon_{\rm H} = -$  0·6, so that it appears that the deposited substance responsible for the persistence of the overvoltage is mainly sodium. The following table gives the quantities of electricity required to remove the active material in the two cases.

	Cathodic Polarisation.	Anodic Break, — o·6 to — o·3.	Ratio.
Purified solution Na <sub>2</sub> SO <sub>4</sub> 10 <sup>-4</sup> N	31 coulombs	6 × 10 <sup>-5</sup> coulombs 3.6 × 10 <sup>-3</sup> ,,	2 × 10 <sup>-6</sup>

If it is assumed that the rate of cathodic deposition of sodium in the mercury is approximately proportional to its concentration, the ratio of amount deposited (= anodic break) to the amount of cathodic polarisation should be proportional to the concentration of sodium ions in the solution, which is thus of the order of  $2 \times 10^{-6} N$ , or  $5 \times 10^{-8}$  gms. per c.c. in the "purified" solution.

Similar experiments were made on the decay of the hydrogen overvoltage at platinum electrodes. The overvoltage is much smaller with this metal and a much more limited range of potentials is open to observation. Some typical curves obtained are shown in Fig. 1. It is evident that at these potentials, which are near the reversible hydrogen potential of the solution, the rate of decay of the overvoltage is considerably less than the theoretical. It follows that the rate of decay is not governed solely by the transfer of electrons from the metal to the solution, but is influenced by a reverse process, which helps to maintain the overvoltage. This probably arises from the electromotive activity of hydrogen dissolved in or adsorbed on the platinum.

Decay of the Oxygen Overvoltage at Platinum Electrodes.—Similar experiments were made on the decay of the oxygen overvoltage



-  $\circ$   $\cdot$  4  $\times$  10<sup>-3</sup> amp. for 10 mins.

after anodic polarisation in dilute sulphuric acid containing oxygen. Some of the curves obtained are shown in Fig. 3. Up to 100 seconds the slope of the  $V-\log t$  curve is somewhat less than the theoretical, but between 100 and 1000 seconds good agreement with the theoretical slope was obtained  $(\Delta V/\Delta \log_{10} t = 0.120)$ . The discrepancy in the earlier stages of the decay is not sufficiently well marked to permit any definite conclusion as to its cause. It may however be due to a slight electromotive activity by the oxygen formed in the electrolysis, which remains for a time (about one minute) and then disappears.

#### Summary.

1. An expression for the rate of decay of hydrogen and oxygen overvoltages, when uninfluenced by the electromotive activity of any products of the electrolysis, is obtained.

2. The theoretical relation has been realised for the hydrogen overvoltage at mercury electrodes, when the initial potential of the electrode was not much more negative than  $\epsilon_{\rm H} = -1$  o volts. It is concluded that the hydrogen formed in the electrolysis has no appreciable electromotive activity at potentials more negative than  $\epsilon_{\rm H} = -0.33$ .

3. When the original potential of the electrode is considerably more negative than - 1.0 volts, much smaller rates of decay were observed, which are due to the deposition of minute amounts of metallic impurities in the mercury. At platinum electrodes, the rate of decay near the reversible hydrogen potential is considerably less than the theoretical, owing probably to the electromotive activity of hydrogen dissolved in or adsorbed on the metal.

4. The rate of decay of the oxygen overvoltage at platinum electrodes is somewhat slower than the theoretical for the first 100 seconds, but between 100 and 1000 seconds good agreement with the theoretical rate was obtained.

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## A NOTE ON THE DISSOCIATION PRESSURE OF STRONTIUM CARBONATE.

By John Chipman.

Received 17th July, 1933.

The first accurate measurements of the dissociation pressure of strontium carbonate were made by Jones and Becker.1 Their data were subsequently used by Becker 2 in studying the equilibrium in the reaction

$$Fe_3C + CO_2 = 3Fe + 2CO$$
 . . . (1)

In these experiments the pressure of carbon dioxide was fixed by the presence of both strontium oxide and carbonate so that a measurement of the total pressure furnished a simple method of determining the composition of the gas. The usefulness of Becker's data in establishing the free energy of iron carbide depends upon an accurate extrapolation of the dissociation pressure. The method of extrapolation employed by Jones and Becker cannot be considered accurate.

Recently Tamaru and Siomi<sup>3</sup> determined the dissociation pressures up to one atmosphere at 1250° C. The upper end of the curve is thus well established, but at temperatures below 800° no satisfactory data have been obtained.

Becker measured the total pressure developed in a mixture of graphite, strontium carbonate and oxide. At the higher temperatures these data

<sup>&</sup>lt;sup>1</sup> Jones and Becker, *J. Chem. Soc.*, 2669, 1927. <sup>2</sup> Becker, *J. Iron Steel Inst.* (London), 121, 337, 1930.

<sup>&</sup>lt;sup>3</sup> Tamaru and Siomi, Z. physik. Chem., 159A, 227, 1932.

serve as an excellent check on the directly determined constants of the "producer-gas reaction,"

C (graphite) + CO<sub>2</sub> = 2CO; 
$$K_2 = p^2_{CO}/p_{CO_2}$$
. (2)

At the lower temperatures they may be used to calculate the dissociation pressure of strontium carbonate. Values of  $K_2$  computed from Becker's data above 800° C. may be expressed by the equation: <sup>4</sup>

$$\log K_2 = -8758/T + 2.213 \log T - 0.00105 T + 9.85 \times 10^{-8} T^2 + 3.278$$
.

This expression is used to obtain the values of  $K_2$  given in the second column of Table I. The third column of this table gives the same constant when pressures are expressed in millimeters. The fourth contains Becker's measurements of total pressure in the C—SrCO<sub>3</sub>—SrO mixture and the fifth the calculated pressure of carbon dioxide. The results at the two lowest temperatures are about 30 per cent. lower than were obtained by Jones and Becker's extrapolation.

Temperature °C.	$K_2 = p^2_{\text{CO}}/p_{\text{CO}_2}.$		$p_{\text{co}} + p_{\text{co}_2}$	<i>\$</i> co₂•
	Atm.	mm.	mm.	r CO2.
650 700 750 800	0·300 0·92 2·55 6·45	228 698 1940 4900	2·0 7·0 22·0 66·0	0·017 0·069 0·243 0·86

TABLE I.—Calculation of Dissociation Pressure of Strontium Carbonate at Lower Temperatures.

The dissociation equilibrium cannot be adequately represented by a simple straight-line plot of  $\log p$  against I/T, on account of the large change in heat capacity attending the reaction. The individual specific heats have not been determined, but we are quite safe in assuming that the change in heat capacity is the same as in the decomposition of calcium carbonate. The data assembled by Bäckstrom <sup>5</sup> are not appreciably altered by the newer determinations of Esser, Averdieck and Grass <sup>6</sup> on calcium oxide and spectroscopic data of Gordon and Barnes <sup>7</sup> on carbon dioxide. With sufficient accuracy the change in heat capacity may be represented by a linear expression which differs only slightly from Bäckstrom's equation:

$$SrCO_3 = SrO + CO_2$$
;  $\Delta Cp = 1.2 - 0.0070 T$  (3)

When this is put into the general free energy equation and the result divided by -RT, we have:

$$\log p = -\Delta H_0/4.575 T + 0.604 \log T - 0.000765 T + \text{Const.}$$

A function suitable for plotting against reciprocal temperature is obtained by grouping three of the above terms, thus:

$$\Sigma = \log p - 0.604 \log T + 0.000765 T.$$

<sup>4</sup> Chipman, Ind. Eng. Chem., 24, 1013, 1932.

<sup>&</sup>lt;sup>5</sup> Bäckstrom, J. Amer. Chem. Soc., 47, 2443, 1925.

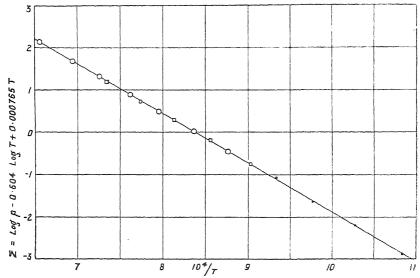
<sup>&</sup>lt;sup>6</sup> Esser, Averdieck and Grass, Arch. Eisenhüttenw., 6, 293, 1933. Gordon and Barnes, J. Physic. Chem., 36, 1143, 1932.

A plot of  $\Sigma$  against I/T is shown in Fig. 1. The four calculated points of Table I, are seen to lie on the straight line passing through the points of Tamaru and Siomi. The line is represented by the expression:

$$\Sigma = -11710/T + 9.810$$

or for pressures in millimeters,

$$\log p = -11710/T + 0.604 \log T - 0.000765 T + 9.810 . (4)$$



Dissociation Pressure of Strontium Carbonate Tamarů & Siomi; 
Jones & Becker; • Calculated Fig. I.

The increase in free energy is given by the expression:

$$SrCO_3 = SrO + CO_2; \ \Delta F^{\circ}_{298\cdot 1} = 42400 \text{ cal}; \Delta F^{\circ} = 53570 - 1\cdot 2 \ T \text{ ln } T + 0\cdot 0035 \ T^2 - 31\cdot 69 \ T$$
 (5)

The heat of dissociation is

$$\Delta H = 53570 + 1.2 T - 0.0035 T^2$$
;  $\Delta H_{298} = 53620$  cal. (6)

This result is compared with the various calorimetric values in Table II.

TABLE II.—HEAT OF DISSOCIATION OF STRONTIUM CARBONATE.

Authority.				Δ	H.
Berthelot 8				53,200	calories.
Thomsen 9		•		53,230	21
Thomsen 10				55,770	,,
de Forcrand 11	•			57,300	,,
I.C.T. 12	•	•	•	56,150	,,
Calculated				53.620	

<sup>&</sup>lt;sup>8</sup> Berthelot, Thermochemie, Gauthier-Villars et Fils, Paris, 1897.

<sup>&</sup>lt;sup>9</sup> Thomsen, Ber., 12, 2031, 1879; J. prakt. Chem. (2), 21, 38, 1880.

<sup>10</sup> Thomsen, Thermochemische Untersuchungen, Barth, Leipsig, vol. 3, p. 259. 1883.

11 De Forcrand, Compt. rend., 146, 512, 1908.

Compt. Tables McGraw-Hill,

<sup>&</sup>lt;sup>12</sup> International Critical Tables, McGraw-Hill, New York, vol. 5, pp. 181, 198, 1929.

Values of the dissociation pressure at round temperatures calculated from Equation 4 are given in Table III. Corresponding values computed from the equations of Tamaru and Siomi and of Jones and Becker are given for comparison. The application of the recalculated values to the study of Becker's data on the equilibrium involving iron carbide will be presented elsewhere.

TABLE	III.—DISSOCIATION	Pressure	OF	STRONTIUM	CARBONATE.
	(1	Millimetres.	)		

Temperature °C.	Recalculated.	Tamaru and Siomi.	Jones and Becker.
650 700 750 800 850 900 950 1000 1050 1100 1150 1200	0.016 0.069 0.25 0.79 2.32 6.08 14.6 32.5 68 134 249 444 755	0.020 0.080 0.278 0.85 2:38 6:10 14:4 31:9 66:5 131 247 445 773	0.023 0.090 0.30 0.91 2.47 6.19 14.4 31.2 64 125 231 411

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# IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS. PART I. COLLOIDAL FERRIC HYDROXIDE.

By B. N. Desai and S. K. Borkar.

Received 4th August, 1933.

Dialysis has been utilised since the time of Graham for freeing a colloidal solution from the impurities necessarily introduced into it at the time of its preparation, viz., the peptising agent and the other electrolytes formed as a result of double decomposition. The importance of the influence of dialysis on the various properties of colloidal solutions has, however, not been generally realised by colloid chemists. No systematic investigations seem to have been made to determine simultaneously the relation between the charge on the particles and the stability, viscosity and other related properties of colloidal solutions dialysed and diluted to different extents. The present investigation was undertaken with a view to study extensively several properties of colloidal ferric hydroxide with reference to the changes in charge on the colloidal particles.

#### Experimental.

Preparation of Ferric Hydroxide Sol.—100 gm. of hydrous ferric chloride were dissolved in 300 c.c. of water. The sol was prepared in instalments of 500 c.c. About 50 c.c. of ferric chloride solution were added to 500 c.c. of boiling distilled water drop by drop, the mixture being stirred all the time. The resulting brown red sol was further boiled

for half an hour.

Dialysis of the Sol.—The sol was dialysed in a parchment paper bag which was previously kept soaked in distilled water for 3 to 4 days. The outer water was changed twice a day. The amount of ferric chloride in the dialysate decreased with progress of dialysis. The amount of colloidal ferric hydroxide was estimated from time to time by adding potassium sulphate in excess to the sol, the resulting coagulum being filtered, washed, dried and weighed as Fe<sub>2</sub>O<sub>3</sub>. The concentration of the colloid is expressed in gms. of Fe<sub>2</sub>O<sub>3</sub> per litre. Samples of sol were withdrawn after different periods of dialysis for experiments on the variation

of its properties with progress of dialysis.

Measurements of Cataphoretic Speed.—The cataphoretic speed was measured by Mukherjee's improved U-tube method. In order to get reliable results, it is necessary, as pointed out by Mukherjee, to have the upper liquid such that the direct and reverse boundary movement as well as the potential gradient before and after the experiment will be the same. Desai, Nabar and Barve 2 have shown that dialysate can be used as a satisfactory upper liquid under certain circumstances in the case of colloidal ferric hydroxide. In the present investigation the upper liquid was prepared by making the dialysate equiconducting with the sol by the addition of a suitable amount of concentrated ferric chloride solution. In all the cases the upper liquid so prepared was found to satisfy the requirements of the constancy of potential gradient both before and after the experiment as well as a close agreement between the direct and reverse movements. The electrodes were put in the side bulbs and not in the limbs of the U-tube in order to avoid the disturbing effect of electrolysis on the sharpness of the boundary. In the results given in this paper, the difference between the direct and reverse movements was never found to exceed 5 per cent., it being about 3 per cent. in most of the cases.

40 c.c. of the colloid required in each experiment were made up by adding 30 c.c. of the colloid and 10 c.c. of water (distilled) or water + electrolyte together. In the experiments for studying the effect of electrolytes on the colloid, the electrolytes were also added to the upper liquid so as to get the same ionic environment. In dilution experiments, sols of different concentrations were prepared by adding requisite amounts

of distilled water to the colloid.

As considerable time was required to complete various kinds of measurements with a sample of the sol dialysed for a particular period, the effect of ageing on the cataphoretic speed was also studied in some cases. On repeating some of the experiments after a period of more than eight weeks, it was found possible to reproduce the results within the limits of experimental error. In all the tables of results, the cataphoretic speed (mean of direct and reverse movements) corrected for viscosity is expressed in centimetres per second per volt per centimetre × 105. The concentration of the electrolytes added is expressed in millimoles per

Determination of Stability.—The stability was determined by finding out the amount of KCl necessary to give instantaneous precipitation

<sup>&</sup>lt;sup>1</sup> Mukherjee, Proc. Roy. Soc., 103A, 102, 1923; Mukherjee, Choudhury and Rai Choudhury, J. Indian Chem. Soc., 4, 493, 1927; Mukherjee, Rai Choudhury and Bhattacharya, ibid., 5, 735, 1928; Mukherjee, Rai Choudhury and Biswas, ibid., 8, 373, 1931; Mukherjee, J. Physic. Chem., 36, 593, 1932.

<sup>2</sup> Desai, Nabar and Barve, J. Indian Chem. Soc., 9, 463, 1932.

of the colloid (flocculation values), the volume of the mixture colloid + electrolyte being kept constant throughout (total volume 20 c.c. = 10 c.c. colloid + electrolyte + water). The flocculation values are expressed in millimoles per litre.

Viscosity Measurements.—Viscosity was determined by using an Ostwald viscometer. The same volume (10 c.c.) of the colloid or the mixture colloid + electrolyte was taken in all the experiments. The time of flow was measured by means of a stop watch reading to one-tenth of a second. The results have been expressed in terms of the viscosity of distilled water at the temperature of the experiment as unity.

Temperature of Experiments.—All the measurements of cataphoretic speed and viscosity were made at a temperature of 30° C. For this purpose, an electrically controlled thermostat with two opposite glass sides was used. The temperature could be maintained correct to within  $\pm$  0·1° C.

#### Results and Discussion.

# (a) Cataphoretic Speed and Stability Determinations of Ferric Hydroxide with the Progress of Dialysis.

The results of cataphoretic speed and stability with the progress of dialysis are given in Table I.

For facility of discussion, the following results have been plotted in

It will Fig. 1.\* be seen that the charge on the particles, assuming that it is represented by the rate of migration, in colloidal ferric hydroxide when it is subjected to dialysis first increases and reaches a maximum after which it gradually decreases. The

TABLE I.

Period of Dialysis.	Concentration of Colloid.	Cataphoretic Speed.	Flocculation Value.
3 days 6 ,, 9 ,, 12 ,, 15 ,, 18 ,, 21 ,,	3.0 2.9 2.9 2.9 2.9 2.9	27·24 43·80 55·65 71·85 68·69 63·84 51·17	550 375 250 100 25 15

flocculation value or the stability of the sol, on the other hand, continuously decreases with the progress of dialysis. These results are similar to those obtained by Desai, Nabar and Barve.<sup>2</sup> The values of cataphoretic speed and stability for sols dialysed for different periods given here are not the same as those obtained by Desai <sup>2</sup> with ferric hydroxide sol dialysed for the same periods probably because of the different rates of dialysis in the two cases. The nature of the curves is, however, the same.

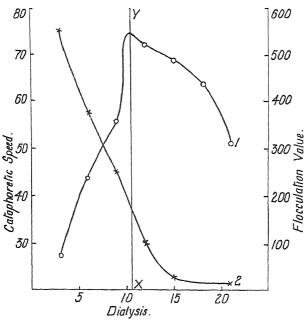
Desai <sup>2</sup> has explained the initial increase in charge with the progress of dialysis as due to "preferential adsorption" (the word preferential indicating that the ions are adsorbed in the inner sheet of the double layer) of the similarly charged ions and the subsequent decrease in charge as due to a continuous decrease of the amount of the peptising agent. The continuous decrease in the flocculation value with the progress of dialysis has been explained on the assumption of certain changes in the preferential adsorption of H and Fe ions in the presence of KCl. No

\* As shown in section (c) the maximum value of cataphoretic speed with the progress of dialysis must have occurred after a dialysis of nine days and before twelve days, the value of the maximum cataphoretic speed being greater than 71.85. It is because of this reasoning that in Fig. 1 the maximum value of cataphoretic speed is shown to have occurred on the tenth to eleventh day of dialysis.

experiments have, however, been performed to test the validity of the above assumptions. In the following tables are given the measurements of cataphoretic speed in the presence of HCl, KCl and HCl + KCl of

colloidal ferric hydroxide dialysed to different extents.

It will be seen from Table II. that the charge on colloidal particles continuously increases up to a certain stage on adding small increasing amounts of HCl and KCl. On the addition of larger amounts of electrolytes, however, the charge begins to decrease. The initial increase in the cataphoretic speed on the addition of an electrolyte is due to preferential adsorption of the similarly charged ion, while the subsequent decrease is due to the preferential adsorption of the oppositely charged ion. Also in all the cases the initial increase in charge is greater with HCl than with KCl. This is probably due to greater adsorption of H ion than K ion in conformity with the strong peptising action of the former



- Cataphoretic speed—dialysis curve.
   Flocculation value—dialysis curve.
  - Fig. 1.

ion. Again in all the cases the concentration of the electrolyte at which the maximum value of charge is reached greater in the HCl case of than ofKCl. This is one should expect in view of greater adsorbability of H ion than  $\mathbf{K}$ ion which will not allow the preferential adsorption of the oppositely charged ion to noticeable be even when larger amounts HC1 than KCl are added.

With the progress of dialysis, the amounts of

stabilising ions, H and Fe, in the sol continuously decrease as both HCl and FeCl<sub>3</sub> pass out in the dialysate. From Table I. it will also be seen that the concentration of the colloid does not change to any appreciable extent with the progress of dialysis. Hence the process of dialysis might be taken roughly as the reverse of the process of adding small increasing amounts of electrolytes to the colloid. If this analogy is correct, one would expect that with the progress of dialysis, the charge on the colloid will first increase and then decrease. On extreme dialysis, the colloid will coagulate due to the removal of the stabilising agent from the double layer. Thus a colloid solution of ferric hydroxide when subjected to dialysis will show first an increase and then a decrease or a continuous decrease in the cataphoretic speed according as whether the amount of HCl and FeCl<sub>3</sub> initially present is more, equal to or less than what would correspond to the maximum in the cataphoretic speed-concentration curve of the sol with those electro-

TABLE II.—Sol B. Concentration 2.98 gms./Litre  ${\rm Fe_2O_3}$  on the Fourth Day of Dialysis.

				DIALYSIS.			
Period of Dialysis of Sol.	Concentra Electro		Cata- phoretic Speed.	Period of Dialysis of Sol.	Concentra Electro		Cata- phoretic Speed.
(1) 4 days	HCl†	0.000	40.92	(3) 18 days	HCl	0.000	52.35
. ,	i '	0.013	41.88	,		0.013	54.38
		0.025	44.86			00.19	58·01
		0.037	50.42			0.025	58.76
		0.050	54.49*			.0037	61.51*
		0.063	48.82	l i		0.050	57.27
		0.075	47.96			0.075	55.12
		0.125	44.23			0.123	51.92
		0.250	41.67		KCl	0.000	52.35
	KCl	0.000	40.92		1101	0.013	55 <sup>2</sup> 4
		0.013	44.13			0.010	55.98
		0.019	47.54			0.025	56.52*
	}	0.025	50.75*			0.037	54.17
		0.037	48.18			0.050	49.15
	1	0.050	46.69		T-itial TTC	1	
		0.125	44.66		Initial HC		o
	ĺ	0.250	37.12		KCI	0.000	54.38
	Initial HC	1-0.005				0.000	55.88
	KCl	0.000	44.86			0.013	59·82 64·10
	IXCI	0.000	45.61			0.023	64.95*
		0.037	46.47*			0.050	60.15
	1	0.050	46.26			0.075	56.62
		0.075	43.25				
			-13 -3		Initial HC		
	Initial HC				KCl	0.000	57.27
•	KCl	0.000	44.53			0.025	57.90
	}	0.013	46.79			0.037	58.43*
		0.025	47.01			0.050	53.20
	}	0·037 0·050	47·64* 44·66	(4) 25 days	HCl	0.000	49.57
		0.030	44 00			0.013	52.88
(2) 8 days	HCl	0.000	62.82			0.025	54.49
., ,		0.013	65.06			0.050	56.62
		0.013	67.30*			0.063	57.58*
		0.025	67.10			0.075	53.3I
		0.037	64.21			0.130	51.48
		0.050	63.66		KCl	0.000	49.57
		0.125	56.72			0.013	53.10
	KCl	0.000	62.82			0.025	54.70
		0.009	65.49*			0.037	55.55*
		0.013	64.10			0.050	53.63
		0.025	61.32			0.125	52.46
		0.050	53.95		Initial HC	1-0:012	
	ĺ	0.125	52.77		KC1	0.000	52.88
	Initial HC	1=0:013			1101	0.013	54.49
	KCl	0.000	65.06			0.025	58.22*
		0.013	65.82			0.037	56.10
		0.019	66.13			0.050	53.50
		0.025	66.56*		T-:4:-1 TTC		
		0.037	64.10		Initial HC		
		0.050	62.92		KCl	0.000	53.31
	Initial LIC	1-0.070				0.013	59.19
	Initial HC KCl	0.000	62.66			0·019 0·025	65·27* 63·66
	17.01	0.000	63·66 64·21			0.025	59.07
		0.000	65.60			0.037	55.01
		0.013	66.56*			2 0 0 0	55 01
		0.025	64.85	BURGOST			
		0.050	58.87				
***************************************	1		3/	<u> </u>	<u> </u>		

<sup>\*</sup> Indicates the highest value of cataphoretic speed obtained in each case.

† On the addition of small increasing amounts of FeCl<sub>3</sub> to colloidal ferric hydroxide, it was also found that in all the cases the cataphoretic speed first

ytes. These results thus fully support the assumption made by Desai 2

in explaining changes in charge on dialysis.

It should, however, be pointed out that the process of dialysis is not exactly the reverse of the process of adding small increasing amounts of the peptising electrolyte to the colloid. For if it were so one would expect that with the samples of the sol dialysed for periods shorter than what correspond to the maximum in the cataphoretic speed-dialysis curve and containing amounts of the peptising electrolyte more than what correspond to the maximum in the cataphoretic speed-concentration curve, the cataphoretic speed should continuously decrease on adding small increasing amounts of the peptising electrolyte. It will, however, be seen from Table II. that with such samples of the sol also the cataphoretic speed has increased at first on the addition of small increasing amounts of the peptising electrolyte. As shown later in this section the cataphoretic speed also increases on the addition of small increasing amounts of KCl to the sol even when an amount of HCl more than what corresponds to the maximum in the cataphoretic speed concentration curve with it (HCl) has been added to the sol in the beginning. The initial increase in the cataphoretic speed observed in the above cases is apparently due to an increase in the preferential adsorption of the similarly charged ions in the presence of the peptising or other electrolyte which has been added subsequently.

In Table III. (this table is constructed from data given in Table II.) are given the values of the maximum cataphoretic speed obtained in presence of HCl, KCl and HCl + KCl in case of sols dialysed to different

extents.

TABLE III.

Period of Dialysis.	Electrolyte.	Concentration at which Maximum Value of Cata- phoretic Speed is Obtained.	Initial Amount of HCl Added.	Maximum Value of Cataphoretic Speed.
4 days	HCl KCl HCl + KCl HCl + KCl	0·050 0·025 	 0·025 0·125	54·49 50·75 46·47 47·64
8 days	HCl KCl HCl + KCl HCl + KCl	0·019 0·009 —	0·013 0·050	67·30 65·49 66·56 66·56
18 days	HCI KCI HCI KCI HCI KCI	· 0·037 0·025 ——	 o·o13 o·o5o	61·51 56·52 64·95 58·43
25 days	HCl KCl HCl + KCl HCl + KCl	o∙o63 o•o37 — —	 0·013 0·075	57·58 55·55 58·22 65·27

The following conclusions can be drawn from the above table:-

<sup>(</sup>I) In all the cases except for the sol dialysed for four days, the maximum value of the cataphoretic speed is higher in the presence of HCl + KCl than with KCl alone.

<sup>HCl + KCl than with KCl alone.
(2) For sol dialysed for twenty-five days, the maximum value of the cataphoretic speed obtained in the presence of HCl + KCl is higher than with either HCl or KCl alone.</sup> 

(3) (a) When an amount of HCl more than what corresponds to the maximum value of cataphoretic speed with it is initially added to the sol, the cataphoretic speed increases in the beginning on adding KCl to the mixture although one would ordinarily expect that in such cases the speed should continuously decrease on the addition of more and more of the same or other electrolyte. (b) The difference between the maximum value of cataphoretic speed in the presence of HCl + KCl and of KCl alone seems to be increasing with the progress of dialysis of the sol in all the cases—the initial amount of HCl added being more than what corresponds to the maximum in the cataphoretic speed-concentration curve of the colloid with HCl. There does not appear any regular behaviour in cases when the initial amount of HCl added is less than what corresponds to the maximum in the cataphoretic speed-concentration curve.

These results support the assumption made by Desai, viz., that on the addition of KCl the preferential adsorption of the similarly charged ions will increase, in explaining the continuous decrease in the flocculation value with the progress of dialysis in spite of a first increase and then a decrease in the cataphoretic speed. Thus we find from 3 (a) that the preferential adsorption of H ion increases in the presence of KCl. From  $\bar{3}$  (b) above, it will further appear that the preferential adsorption of the similarly charged ion is increased in the presence of KCl when the colloid initially contains the amount of HCl more than what corresponds to the maximum in the cataphoretic speed-concentration curve. As stated before, since electrolytes are removed by dialysis, this process can be considered roughly as the reverse of the process of adding small increasing amounts of electrolyte to the colloid. Therefore the other assumption of Desai, 2 viz., that as with the progress of dialysis the concentration of the intermicellary HCl and FeCl<sub>3</sub> decreases the preferential adsorption of H and Fe ions in the presence of KCl will also decrease, is supported to a certain extent by these results.

As mentioned by Desai, Nabar and Barve <sup>2</sup> on p. 469 of their paper, it was observed in some preliminary experiments that the initial preferential adsorption of the similarly charged ion decreases with the progress of dialysis. Subsequent experiments did not confirm the previous results. It will also be seen from results given in Table II. that there is no regular decrease in the preferential adsorption of the similarly charged ion with

the progress of dialysis.

There are probably other factors besides those mentioned above which should also be considered to explain the abnormal behaviour for the portion of the curves to the left of the line XY in Fig. 1. In the case of gold sol, it has been observed by Desai 2 that with the progress of dialysis both charge and stability, as determined by the flocculation value with KCl, first increase, reach a maximum after which both begin to decrease simultaneously. In the case of colloidal ferric hydroxide, the influence of hydration—colloidal ferric hydroxide is undoubtedly highly hydrated when compared with colloidal gold—is also partly responsible for its abnormal behaviour. It is well known that the hydrophilic sols require very large amounts of electrolytes for their coagulation. It will be seen from section (d) that with the progress of dialysis viscosity of colloidal ferric hydroxide first decreases and then increases. Now if viscosity is taken to indicate the effect of hydration (greater viscosity greater hydration and smaller viscosity smaller hydration), the hydration of colloidal ferric hydroxide can be said to be decreasing in the initial stage of dialysis. If this be the case, then in spite of the charge increasing with the progress of dialysis smaller amounts of electrolytes may be necessary for coagulation. It should, however, be stated that the relation between charge and viscosity is not so simple as will be shown in section (d).

Also with the progress of dialysis the size of the particles will to a certain extent continuously increase. It is therefore quite likely that for the portion of the curves to the left of the line XY in Fig. 1, in spite of higher

initial charge smaller amounts of electrolytes may be necessary for coagulation. For what is observed in determining flocculation values is the appearance of turbidity and a smaller amount of electrolyte will be required to produce a given degree of turbidity in a given time in the case of a sol which initially contains particles of bigger size than the sol which contains particles of smaller size. In what way the charge will be affected during dialysis due to a change in the size of particles when the concentration of the intermicellary HCl and FeCl<sub>3</sub> also continuously changes is difficult to say. This point requires a further investigation.

For the portion of the curves to the right of the line XY in Fig. 1, both charge and flocculation value decrease with further progress of dialysis. If stability is considered as directly related to charge, one would expect that the smaller the charge the smaller will be the amount of an

electrolyte necessary for the coagulation of the sol.

It will be clear from the foregoing considerations that in the case of colloidal ferric hydroxide it is not safe to draw conclusions about the charge on colloidal particles from the measurements of stability, as determined from the flocculation values, although in some cases they may afford a correct criterion for the same.

# (b) Measurements of Cataphoretic Speed from the Point of View of Critical Potential.

The changes in the cataphoretic speed till the coagulation point of the colloid was reached with HCl, KCl, MgCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> at two stages of dialysis—one before the maximum value of charge is reached and the other after it—are given on Table IV.

It will be seen that for both the samples of the sol the initial increase in the cataphoretic speed is greater and occurs at a higher concentration in the case of HCl than with KCl. This is due to greater preferential adsorption of H ion than K ion as stated in section (a). It will also be seen that the initial increase in speed is greater in the case of MgCl<sub>2</sub> than in the case of KCl. This is probably due to greater adsorption of Mg ion than K ion. One can possibly ascribe the greater adsorption of Mg ion than of K ion to a difference in their valency.<sup>3</sup>

The initial increase in the cataphoretic speed is not obtained in the se of  $H_2SO_4$ ,  $K_2SO_4$  and  $MgSO_4$  when small increasing amounts of these actrolytes are added to the colloid. This is not surprising in view of the fact that  $SO_4$  ion has a very large coagulating power. In these cases the preferential adsorption of the similarly charged ion is not allowed to be noticed at all as in the case of electrolytes containing univalent coagulating ion— $SO_4$  ion is preferentially adsorbed from the beginning due to its large coagulating power. These results therefore support the view that the preferential adsorption of the similarly charged ion is noticeable only in those cases when the electrolyte contains univalent coagulating ion.<sup>4</sup>

From Table IV. it will be seen that except in the case of HCl, the value of cataphoretic speed at which coagulation begins is almost the same in case of both the samples of the sol although they had different initial cataphoretic speeds—38·16 in the case of sol dialysed for eight days and 53·42 in the case of sol dialysed for twenty-five days. The difference in the stage of dialysis, i.e., whether the sample of the sol refers to the stage before or after the maximum value of charge on dialysis is reached does not appear to affect the value of the critical charge in the case of colloidal ferric hydroxide. It is also interesting to note that although the colloid begins to coagulate at almost the same value of the charge, the amounts of electrolyte necessary to lower the charge to critical value are not the same.

<sup>&</sup>lt;sup>3</sup> Desai, Koll. Chem. Beih., 26, 409, 1928.

TABLE IV.—Sol C. Concentration 3:00 gms./litre  $\mathrm{Fe_2O_3}$  on the Eighth Day of Dialysis

	Sol Dialysed	for 8 Days.	Sol Dialysed	for 25 Days.	
	Concentration of Electrolyte.	Cataphoretic Speed.	Concentration of Electrolyte.	Cataphoretic Speed.	
HCI	0.000 0.063 0.094 0.125 0.250 0.750 1.250 25.000	38·16 43·59 45·72* 44·01 39·42 36·11 35·46 33·97 33·12*	0.000 0.013 0.019 0.037 0.075 0.125 0.250 2.500 25.000 50.000 100.000	53·42 56·83 59·82* 55·34 53·84 47·64 46·81 46·15 45·72 43·48 42·20 34·82 32·58*	
KCl 0.000 0.025 0.075 0.125 0.190 0.250 0.500 1.250 5.000 50.000 125.000 MgCl <sub>2</sub> 0.000 0.031 0.063 0.125 0.250 0.370 1.250 2.500 25.000 50.000		38·16 40·60 43·55* 41·67 33·97 32·48 32·16 31·84 31·52 28·42*	0.000 0.013 0.019 0.125 0.250 1.250 5.000 15.000	53.42 57.16* 56.40 45.19 42.31 38.57 28.74 26.71 26.50*	
		38·16 39·85 42·52 44·44* 39·14 34·72 31·62 30·98 26·93 26·50*	0.000 0.019 0.025 0.125 0.250 0.370 0.500 0.750 1.250	53.42 57.90* 56.10 53.95 41.13 34.82 32.37 30.12 25.31*	
H <sub>2</sub> SO <sub>4</sub>	0.0000 0.0007 0.0025 0.0250	38·16 37·92 30·45 27·24*	0.0000 0.0025 0.0125 0.0250 0.0500	53:42 50:86 40:60 32:91 28:31*	
K₂SO₄	0.0000 0.0007 0.0025 0.0125 0.0250	38·16 36·76 35·26 29·59 26·17*	0·0000 0·0025 0·0125 0·0200 0·0250	53·42 51·59 38·46 30·98 27·35*	
MgSO <sub>4</sub>	0.0000 0.0007 0.0025 0.0250 0.0500	38·16 35·15 32·58 30·98 28·70*	0·0000 0·0025 0·0125 0·0250	53·4² 50·54 38·03 29·06*	

<sup>\*</sup> In the case of HCl, KCl and MgCl<sub>2</sub> the first asterisk indicates the maximum value of cataphoretic speed obtained and the second asterisk the cataphoretic speed at which the sol begins to coagulate. In the case of H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub> the asterisk indicates the value of charge at which the sol begins to coagulate.

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The higher value of critical charge with HCl than with other electrolytes tried in these investigations is probably due to marked preferential adsorption of H ions. It is, however, to be noted that even in this case the value of the cataphoretic speed at which the coagulation begins is almost the same for the sol dialysed for eight days and twenty-five days and having different initial cataphoretic speed.

Powis 5 working on arsenious sulphide sol found that although there was good agreement in the value of critical potential with electrolyte having multivalent coagulating ions, the same was not found to be the case with electrolytes having univalent coagulating ions. Freundlich 6 has ascribed this anomaly in the case of univalent coagulating ions to the influence of hydration of the colloid particles and has further stated that markedly electrocratic sols will show a uniform behaviour with univalent as well as multivalent coagulating ions. It will be agreed that ferric hydroxide is distinctly more like hydrophilic sols as far as hydration is concerned. However the value at which the coagulation begins is almost the sample with all the electrolytes tried except HCl. The influence of hydration thus does not appear to be playing an important part in the case of colloidal ferric hydroxide. On the other hand, the suggestion of Desai <sup>7</sup> that the value of the critical charge may be different for the same sol when it is coagulated by electrolytes containing same univalent coagulating ion but similarly charged ions of markedly different peptising action seems to be supported by these observations. The doubts expressed by Mukherjee and co-workers 8 about the existence of critical potential characteristic of coagulation of colloid by electrolytes do not seem to be justified in the case of colloidal ferric hydroxide.

#### (c) Cataphoretic Speed Measurements of Ferric Hydroxide Sol Dialysed and Diluted to Different Extents.

The results of these experiments are given in Table V.

Period of Dialysis.	3 Day	s.	6 Day	s.	g D	ays.	12 D	ays.	15 D:	ıys.	18 D	ays.	21 D	ays.
Dilution.	ı.	2.	ı.	2.	ı.	2.	ı.	2.	1.	2.	Ι.	2.	I.	2.
0 2 4 6 10 15 20	27·24 43·27 45·40 41·43 42·09 — 40·70		62.61	_	58.55	85.0 75.0	69·55 68·58 66·88 54·17 54·45	60.0 45.0 30.0 25.0 22.0	68·69 65·10 57·00 56·03 49·68 48·18 45·13	17.5 12.5 11.0 7.0 6.3	60·57 54·17 49·95 44·01 39·69	mounted  mounted  mounted  mounted  mounted	51·17 48·61 42·94 38·99 37·80 37·00 36·96	9.0 6.5 5.0 4.5 4.0

TABLE V.\*-Sol A.

For facility of discussion the results of dilution experiments have been divided into two types according as whether the charge on dilution first increases and then decreases and remains almost constant thereafter or first decreases and remains almost constant thereafter. These are plotted

<sup>\*</sup> In column 1 are given the values of cataphoretic speed, while in column 2 are given the flocculation values with KCl.

<sup>&</sup>lt;sup>5</sup> Powis, J.C.S., 109, 734, 1916. <sup>6</sup> Freundlich, Colloid and Capillary Chemistry, 1926 Edition, p. 419.

<sup>&</sup>lt;sup>7</sup> Desai, J. Bombay Univ., I, (2), 25, 1932.

<sup>8</sup> Mukherjee, Rai Choudhury and Rao, J. Indian Chem. Soc., 5, 697, 1928;
Mukherjee, Choudhury and Rai Choudhury, ibid., 4, 493, 1927; Mukherjee and Rai Choudhury, Nature, 122, 960, 1928.

in Figs. 2 and 3. Cataphoretic speed has also been plotted for the different

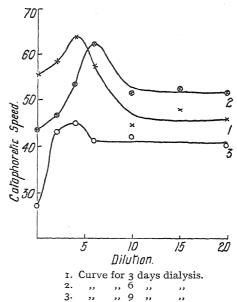
samples of the sol (different dilutions) against dialysis in Figs. 4 and 5.

The flocculation values with KCl for sols diluted to different extents and dialysed for different periods continuously decrease with an increase in dilution. Colloidal ferric hydroxide when coagulated with KCl thus behaves normally to the dilution rule, viz., that the greater the concentration of the colloid the greater the

amount of electrolyte necessary to coagulate it.

It will be seen that in the case of sols dialysed for three, six and nine days on diluting the sol the cataphoretic speed first increases, reaches a maximum value, then decreases and tends to become constant there after (Fig. 2). The maximum value of cataphoretic speed on dilution occurs between dilution 4 and 6 inthese cases. the other hand, in the case of sols dialysed for twelve, fifteen, eighteen and twentyone days (Fig. 3) the charge decreases in the beginning and shows a tendency to become constant thereafter on further dilution.

The maximum value of cataphoretic speed is seen to occur at the stage of twelve days dialysis (Table V.). It is likely that it might have occurred either before or after twelve days dialysis. However, in view of the fact that the sol dialysed for twelve days behaves on dilution similar to the samples dialysed for fifteen, eighteen and twenty-one days, one may be inclined to the view that the maximum value of cataphoretic speed might have occurred after a dialysis of nine days and before the twelfth day, the value of the cataphoretic speed corre-



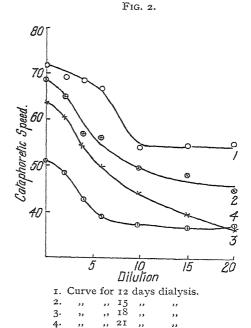
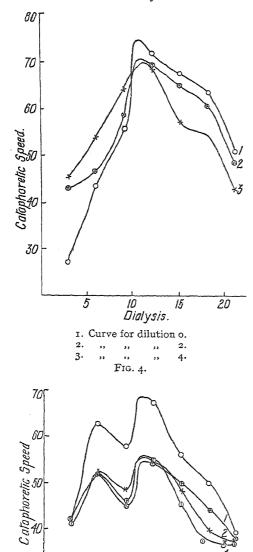


Fig. 3.

sponding to the dialysis of twelve days actually lying on the part of the cataphoretic speed dialysis curve after the maximum. It thus appears

that in the case of ferric hydroxide at least the manner in which changes



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3.

4.

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Dialysis.

1. Curve for dilution 6.

,, Fig 5. will take place in the cataphoretic speed on dilution can indicate whether any particular sample of this sol has been dialysed for a period more or less than the period corresponding to the maximum value of cataphoretic speed on dialysis. As shown in section (a) this sol shows an abnormal behaviour as far as the relation between charge and stability is concerned till the period of the maximum value of charge on dialysis reached. It will be interesting to know if the behaviour of cataphoretic speed on dilution of any one sample of a sol can enable us to know whether the sample falls on one or the other side of maximum of the cataphoretic speeddialysis curve. Further investigation of different sols from this point of view is necessary to see if this particular behaviour is a general property of colloids.

From Table V. it will be seen that the nature of curves obtained by plotting cataphoretic speed against dialysis of sols having same dilution is not the same in all the cases. is observed that in the case of sols having dilution o, 2 and 4 the charge first increases, reaches a maximum value and then de creases (Fig. 4). On the other hand, in the case of sols having dilution 6, 10, 15 and 20 (Fig. 5) there is also a second maximum point in the cataphoretic speed dialysis curve for a period corresponding to six days dialysis. It is, however, to be noted that for dilutions almost a regular behaviour is shown

by a sol dialysed for twelve days or more. The causes of the second maximum point in the case of sols having dilutions 6, 10, 15 and 20 are not quite clear. Dilution

20

15

TO.

15.

20.

of the colloid may give rise to many complications. For example dilution with the dispersion medium may actually give rise to a peptising action and this effect is specially marked with hydroxide sols as observed by Linder and Picton. Also the concentration of the "active electrolyte" will change with dilution and this may ultimately affect the distribution in the double layer. But why these factors should affect only dilutions greater than 4 and that too for a period of dialysis of six days only is difficult to understand from the present results.

The flocculation values (Table V.) show a regular behaviour in all the cases, there being a gradual decrease with an increase in the period of

dialysis.

The nature of charge-dilution curves (Fig. 2) is somewhat similar to the charge dialysis curve (Figs. 1 and 4), and one may be inclined to think that the processes of dilution and dialysis are similar. It is seen that the initial increase in the cataphoretic speed on dilution is noticeable only in the case of sols dialysed for three, six and nine days. The maximum value of cataphoretic speed having occurred at a period of about ten days dialysis, it is certain that the samples of the sol dialysed for shorter periods will contain an amount of the stabilising agent (HCl and FeCl<sub>3</sub>) which is more than what would correspond to the maximum in the cataphoretic speed-concentration curve of the colloid with these electrolytes. As stated in section (a) if a colloid initially contains an amount of the stabilising agent which is more than the maximum in the cataphoretic speed-concentration curve, on dialysing, the charge on the colloid will first increase and then decrease. Just as with the progress of dialysis the amount of the "active electrolyte" continuously decreases, dilution also brings about a decrease in the concentration of the active electrolyte. It is therefore likely that if a sample of the sol initially contains an amount of the stabilising agent which is more than what corresponds to the maximum in the cataphoretic speed-concentration curve (this is certainly the case in the sols dialysed for three, six and nine days as stated above), on diluting it the charge will first increase and then decrease. what is observed in Fig. 2. In the case of the sols dialysed for twelve, fifteen, eighteen and twenty-one days (Fig. 3) the cataphoretic speed does not show an initial increase on dilution. In these cases the amount of the "active electrolyte" is less than what corresponds to the maximum in the cataphoretic speed-concentration curve. As stated in section (a) under the circumstances the cataphoretic speed will regularly decrease on dialysis. Now dialysis and dilution being similar specially as regards the changes in the concentration of the active electrolyte, the sols dialysed for twelve, fifteen, eighteen and twenty-one days should show a decrease in the cataphoretic speed on dilution (Fig. 3).

If the analogy between the processes of dilution and dialysis given in the preceding paragraph is correct, one should also expect that the maximum value of cataphoretic speed should occur at smaller and smaller dilutions with the progress of dialysis. A tendency to this effect is noticeable in the case of sols dialysed for six and nine days; in the former case the maximum cataphoretic speed occurs at a dilution of 6 while in the latter at a dilution of 4. In the case of the sol dialysed for three days

the maximum value, however, also occurs at a dilution of 4.

How far dialysis and dilution can be strictly compared is, however, difficult to say. For although the concentration of the "active electrolyte" changes in both the cases, the concentration of the disperse phase does not change during dialysis while on dilution it changes to the same extent as the active electrolyte. Moreover, as stated before, dilution may give rise to peptisation as well as a decrease in the size of the particles due to the action of the dispersion medium while dialysis may give rise to aggregation of particles and a consequent increase in their size.

 $<sup>^9</sup>$  Linder and Picton, J. C.S., 87, 1926 et seq., 1905; also see Freundlich and Leonhardt, Koll. Chem. Beih., 7, 172, 1915.

From Table V. (also see Figs. 2 and 3) it will be seen that there is a tendency for the cataphoretic speed to become constant at higher dilutions. It has been shown above that dialysis and dilution are similar as regards changes in the concentration of the "active electrolyte." In section (a) it has also been stated that on carrying the dialysis to extreme the stabilising electrolyte is removed from the double layer and therefore the charge decreases to such a low value as to coagulate the sol. On extreme dilution, however, a similar process of removing stabilising agent from the double layer possibly does not take place and therefore the cataphoretic speed remains constant at large dilutions. Also the point where the charge does not further decrease on dilution possibly corresponds to the stage when the amount of the "active electrolyte" still remaining becomes negligible. Further for dialysis for a period longer than twenty-one days (say twenty-five to thirty days) the amount of "active electrolyte" still remaining in the sol will be negligible and stabilising agent would have begun being removed from the double layer; for such samples of the sol the charge may not decrease at all on dilution but remain practically the same at all dilutions. A tendency for this type of effect is noticeable in the results given in Table V., for the cataphoretic speed becomes constant at smaller dilutions in the case of sols dialysed for twenty-one days than with sols dialysed for twelve, fifteen and eighteen days. The stage of dialysis at which the cataphoretic speed does not decrease but remains practically the same on dilution may be termed the "critical point of dilution." As stated in section (b) the cataphoretic speed at which the coagulation begins in the case of ferric hydroxide (stage corresponding to the first critical potential of Freundlich) is about 28 and it is likely that the value of the cataphoretic speed corresponding to the "critical point of dilution "will in most cases be larger than the above value (i.e., 28 in the present case). It will be interesting to investigate different sols on dilution from this point of view.

Finally it may be stated that in the case of ferric hydroxide sol the behaviour to the dilution rule as determined by flocculation values with electrolytes should not be explained by assuming changes in charge produced on dilution, thinking that the stability results always indicate changes in charge. For it has been shown in these measurements that for ferric hydroxide although on dilution stability continuously decreases in all the cases the changes in charge on dilution are not regular.

### (d) Measurements of Viscosity and Cataphoretic Speed of Ferric Hydroxide Sol with the Progress of Dialysis and in the Presence of HCl and KCl with Samples of the Sol Dialysed to Different Extents.

The results of these experiments are given in Tables VI. and VII. It will be seen from Table VI. that with the progress of dialysis the cataphoretic speed first increases, reaches a maximum and then begins to decrease. The viscosity, on the other hand, first decreases, reaches a minimum and then increases. It must, however, be noted that the maximum value of cataphoretic speed and the minimum value of viscosity do not occur simultaneously at the same stage of dialysis of the sol. With highly concentrated sols of Fe(OH)<sub>3</sub>, which show a great tendency to gelation, the viscosity continuously increases with the progress of dialysis. (Desai, Special Number of the Indian Chemical Society, 1933, p. 37.)

From Table VII. it will appear that in the case of sol dialysed for six days the maximum value of cataphoretic speed and the minimum value of viscosity occur simultaneously when small increasing amounts of HCl are added to the colloid. In the other three cases, the minimum value

<sup>&</sup>lt;sup>10</sup> Dhar and co-workers, J. Physic. Chem., 31, 187, 666, 1927, and earlier papers. Also see in this connection Desai, Current Science, 1, 125, 1932, in which article Dhar's view has been criticised.

of viscosity and the maximum value of cataphoretic speed do not occur simultaneously.

There are two different views at present about the relation between charge and viscos-

ity. According to v. Smoluchowski 11 the movement of electrically - charged particles of a sol causes the development of an electric field, which hinders the flow of the sol resulting in an increase of its viscosity. He also observed that a sol with greater electric charge shows greater viscosity

TABLE VI.—Sol D. Concentration 2.80 gms./Litre  ${\rm Fe_2O_3}$  on the Second Day of Dialysis.

Period of Dialysis.	Viscosity.	Cataphoretic Speed.
2 days	1.042	39.53
4 ,, 6 ,,	1.034	46.15
	1.031	49.57
8 ,,	1.023	50.31
10 ,,	1.013*	51.48
12 ,,	1.025	52-24*
15 ,, 18 ,,	1.030	51.81
18 ,,	1.035	49*25
21 ,,	1.042	48-51
24 ,,	1.045	47.75

than a sol containing particles of feeble electric charge. On the other hand, Dhar and co-workers 12 have tried to show from experimental results with a number of sols that the view of v. Smoluchowski is untenable. They conclude that other things being identical, a decrease in the electric charge on colloid particles causes an increase in hydration and necessarily in the viscosity of the sol.

TABLE VII.—Sol. E. Concentration 2.90 gms./Litre  $\mathrm{Fe_2O_3}$  on the Sixth Day of Dialysis.

		6 Days Dialysis	š.	21 Days Dialysis.			
	Concentration of Electrolyte.	Viscosity.	Cataphoretic Speed.	Concentration of Electrolyte.	Viscosity.	Cataphoretic Speed.	
HCI	0.000	1·035	37·39	0.000	1·053	40·70	
	0.025	1·034	38·46	0.025	1·047*	45·72	
	0.050	1·024*	39·85*	0.050	1·052	49·78	
	0.075	1·037	36·71	0.075	1·055	54·49*	
	0.125	1·042	32·91	0.125	1·056	53·50	
KCI	0.000	1·035	37·39	0.000	1·053	40·70	
	0.013	1·030	38·24	0.025	1·040	44·86	
	0.025	1·020*	38·46	0.050	1·036*	47·11	
	0.050	1·024	39·10*	0.075	1·043	50·20*	
	0.075	1·031	35·04	0.125	1·048	47·00	

From the results presented in this section, it will appear that the view of Dhar is not completely supported. The theory of v. Smoluchowski is also not supported by these results.

<sup>\*</sup> Indicates minimum value of viscosity and maximum value of cataphoretic speed.

<sup>&</sup>lt;sup>11</sup> v. Smoluchowski, Koll. Z., 18, 194, 1916; Kruyt, Koll. Chem. Beih., 28-1, 1929; ibid., 29, 413, 1929; also see Wo. Ostwald, Handbook of Colloid Chem istry, 1919 Edition p. 180

istry, 1919 Edition, p. 180.

12 Dhar and co-workers, J. Physic. Chem., 30, 1646, 1926; Z. anorg. Chem., 152, 393, 1926; Koll. Z., 42, 124, 1927; ibid., 48, 43, 1929; J. Indian Chem. Soc., 6, 641, 1929; ibid., 9, 315, 441, 455, 1932.

In a recent note in Current Science, Desai 10 has reported that although with the progress of dialysis of colloidal thorium hydroxide viscosity continuously increases, the cataphoretic speed first increases, reaches a maximum and then decreases. Discussing these results from the point of view of various factors, viz., (1) Electro-viscous effect, (2) Hydration, (3) Structure and shape of particles, and (4) Electrolyte content, Desai has concluded that neither the view of v. Smoluchowski nor of Dhar can individually explain the changes in charge and viscosity with the progress of dialysis in the case of thorium hydroxide sol.

It must be stated that Dhar has drawn conclusions about changes in charge from the viscosity and flocculation value determinations; he has not determined the cataphoretic speed of colloidal solutions under different conditions, although those measurements alone can give an idea about changes in charge. As shown here it is unsafe to draw conclusions about changes in charge on colloidal particles from viscosity measurements just as in the case of flocculation values, for although in some cases they may afford a correct criterion they are likely to lead to erroneous conclusions in other cases.

#### Summary.

Colloidal ferric hydroxide has been studied from different points of view. The following results have been obtained:—

(a) With the progress of dialysis the cataphoretic speed first increases, reaches a maximum value and decreases thereafter, while stability as determined by flocculation values with KCl continuously decreases. The results have been explained on the basis of changes in the "preferential adsorption" of similarly charged ions. The influence of hydration and changes in the size of particles with the progress of dialysis has also been considered.

(b) Sols having different initial cataphoretic speeds are found to begin to coagulate at the same value of the cataphoretic speed. Departures in certain cases have been explained on the view of "preferential adsorp-

tion " of similarly charged ions.

(c) Stability determinations with KCl show that the sol is normal to dilution rule. Changes in cataphoretic speed are not found to be regular. In the sols dialysed for periods shorter than what correspond to the maximum in the cataphoretic speed-dialysis curve, the charge on dilution first increases, then decreases and tends to become constant thereafter; for sols dialysed for longer periods the charge first decreases and tends to become constant thereafter. These changes in cataphoretic speed on dilution are explained by assuming similarity between processes of dilution and dialysis.

(d) Viscosity and cataphoretic speed determinations show that neither the view of v. Smoluchowski nor of Dhar can individually explain the

results.

#### Conclusion.

It is erroneous to draw conclusions about changes in charge on the colloidal particles from the results of stability and viscosity determinations in the case of ferric hydroxide sol. For although in some cases they afford a correct criterion, in others they do not support the same relation between charge, stability and viscosity. Also as far as this sol is concerned, the idea of critical potential is supported.

The authors wish to thank Professor A. R. Normand for interest in the work and some valuable suggestions, Dr. T. R. Bolam (Edinburgh) for helpful criticism of the paper, and Mr. G. M. Nabar for the useful halp in the continuous state.

help in the preliminary stage of the work.

Note.—In section (a) it has been stated that in so far as the removal of the peptising electrolyte is concerned, the process of dialysis can be taken as a reverse of the process of adding small increasing amounts of the peptising electrolyte to the colloid. It should, however, be stated that during dialysis both hydration and the size of the colloidal particles also change besides the amount of the peptising electrolyte. It is therefore likely that on adding small increasing amounts of the peptising electrolyte to the sols, the hydration and the size of the particles may not be brought back to the same stage as in the undialysed sol. If this be the case, the adsorption of the ions will also be affected and with it the cataphoretic speed. Under the circumstances, it may not be possible in practice to obtain the actual reverse of dialysis on adding small increasing amounts of the peptising electrolyte to the colloid although the analogy may be quite correct in so far as the question of removal of the peptising electrolyte during dialysis is concerned.

According to Pauli and Walter, 18 on diluting a sol the aggregates are broken down giving greater number of colloidal ions; and this effect might be responsible for abnormal rise in colloidal ion mobility on dilution. It should be stated that the present results on dilution cannot be explained on the basis of their view; our results can be explained easily as shown in section (c) by assuming similarity between the processes of dilution and. dialysis.

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13 Knoll. Chem. Beih., 17, 256, 1923.

# A CONTRIBUTION TO THE THEORY OF LIQUID VISCOSITY.\*

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The earlier kinetic treatments of liquid viscosity, based on an analogy between the mechanism of gaseous and liquid viscosity, as well as the later elastic wave mechanism treatment of Brillouin, and mixed quantum mechanics and kinetic derivation of Phillips 2 all lead either to a positive temperature coefficient (which is negative for liquids) or to unfeasible functions. Moreover the volume functions, developed by Faust,3 Batchinski,4 and MacLeod,5 have failed to represent high pressure data. On the other hand investigators,6 employing as part of their

<sup>\*</sup>Contribution from the Chemistry Department, Washington Square College, New York University.

<sup>&</sup>lt;sup>1</sup> L. Brillouin, J. Physique et Rad., 3, 326, 1922.

<sup>2</sup> H. B. Phillips, Proc. Nat. Acad. Sci., 7, 172, 1921.

<sup>3</sup> O. Faust, Z. physik. Chem., 86, 479, 1914.

<sup>4</sup> A. Batchinski, Z. physik. Chem., 84, 643, 1913.

<sup>&</sup>lt;sup>5</sup> D. B. MacLeod, Trans. Faraday Soc., 19, 6, 1923; 21, 151, 1925.

<sup>6</sup> O. Guzman, Ann. Soc. Espan. de Fisica y Quimica, 11, 353, 1913; Drucker, Z. physik. Chem., 92, 287, 1918; C. V. Raman, Nature, 111, 532, 1923; J. S. Dunn, Trans. Faraday Soc., 22, 401, 1926. This derivation is semi-kinetic; E. N. Andrade, Nature, 125, 489, 1931; S. E. Sheppard, J. Rheology, 1, 349, 1931; M. P. J. Iyer, Ind. J. Physics, V, 14, 371, 1930; E. L. Lederer, Kolloid Beihefte, 34, 270, 1931.

attack concepts of thermodynamics, have been particularly successful, and have obtained an equation of the general type,

$$\eta = AT^{-c}e^{(F/T + DT)} \qquad . \tag{I}$$

where  $\eta$  is the coefficient of viscosity, T the absolute temperature, e the natural base, c and D constants which may equal zero according to the theory, F a constant generally expressing the heat of dissociation of complexes in a liquid, and A a constant in Raman's theory expressing the viscosity of the vapour.

Recently, the kinetic treatment \* has been revived by E. Madge, 7 who redirected attention to Maxwell's equation. 8 The latter considered a liquid to be the limiting case of an elastic solid in which the rate of disappearance of the elastic stress would be proportional to the stress, and the rate of appearance of the strain, or velocity gradient in the case of viscosity, would be constant. He concluded that,

$$\eta = Et \qquad . \qquad . \qquad . \qquad (2)$$

where  $\eta$  is the coefficient of viscosity, E an elasticity modulus, and t, "the relaxation time of elastic force," is the time it takes the force to decrease 1/eth its value, that is, the time the body sustains a stress. Madge evaluates (2) first by assuming that the equation of Miss Tilliard developed for the elasticity of metals can be extended to liquids,

$$E = A_1 e^{-CT} . (3)$$

where  $A_1$  is a proportionality constant and C the reciprocal of the "temperature of fusion." Further he assumes arbitrarily that t follows the function, according to Graetz,

$$t = \frac{M}{T - b} \quad . \tag{4}$$

where M is a constant and b the "temperature of complete solidification." Substituting (3) and (4) in (2), and calling the product of M and  $A_{\mathbf{I}}$  the constant A,

$$\eta = \frac{Ae^{-CT}}{T - b} \quad . \quad . \quad . \quad (5)$$

It is clear that, due to the arbitrary character of the substitutions (3) and (4), the physical interpretation of (5) is limited, in that its relation to Maxwell's original equation is dubious. It is, therefore, the aim of the present investigation to evaluate equation (2), which is accepted as the correct representation of liquid viscosity, in such a form that it may be tested and given a physical significance. To do this it is necessary (1) to formulate some definite kinetic picture of the liquid state from which the relaxation time may be deduced, (2) to relate the elasticity modulus to some measurable quantities of the liquid, and (3) to perform the proper algebraic substitutions for E and t. Further consequences for viscosity under pressure are deduced in section II.

\* There is also a highly mathematical but unmanageable derivation of M. Satô, based upon the Debye dipole structure of the liquid molecule: Tohoku Imp. Univ. Jour., Sci-Rep., 1, 14, 405, 1925. His equation is

$$\eta = \frac{\pi c l}{48} \cdot \frac{\rho^{5/3}}{(m_{II} w)} \cdot \sqrt{T} \cdot \sum \frac{\mu^{4n} P_n}{(kT)^{2n}} \cdot \frac{1}{r_0^{(6n-3)}}$$

<sup>E. Madge, J. Physic. Chem., 34, 1599, 1930.
C. Maxwell, Phil. Mag. (4), 35, 133, 1868.</sup> 

#### I. Evaluation of Maxwell's Equation.

I. The equation (2) itself suggests that there exists in the liquid some structure, which breaks down and builds up periodically, capable of having elastic properties. The above mentioned investigators in the "thermodynamic" treatment of viscosity have all been led to assume in a liquid the presence not only of simple molecules but also of transitory "associated" complexes. Further the work of Stewart on cybotaxis has rather conclusively shown that there must be some such intermittent "associated" groups to account for solid-like X-ray halos. Since these groups have some properties similar to crystals it is natural to accept them as being the ones responsible for elastic properties. No assumptions need be made as to their specific size, or as to the nature of the binding; all that is here required is that they should be able to sustain a stress for the brief time of their existence.

One must further assume a mechanism for the joining and disjoining of these groups. The simplest hypothesis is that the groups exist by virtue of possessing less kinetic energy than the potential necessary for their "association." Thus an ordinary Boltzman application, if it holds for the liquid state, will give the distribution at any instant of the respective types of molecules. Moreover it follows that the groups are temporary due to the disruptive action of simple molecules, which possess greater kinetic energy.

The relaxation time, it has been noted, is the time the body sustains a stress. According to the view just stated, this would be the average time an associated group exists. In terms of collision frequencies, it depends upon the average number of collisions per second that a group suffers from the simple molecules, or the total number of groups divided by the total frequency of collision between the two types of molecules. Jeans 10 in his Dynamical Theory of Gases gives this expression for the frequency of collision between two types of molecules in the gaseous state.

$$2N_1N_2\left(\frac{\sigma_1+\sigma_2}{2}\right)^2\sqrt{2\pi RT\left(\frac{m_1+m_2}{m_1m_2}\right)}$$

N represents the molecular density,  $\sigma$  the molecular diameter, m the mass, R the gas constant, T the absolute temperature, and if this should be extended to the liquid state the subscripts I and 2 the properties of complexes and simple molecules respectively. It is unreasonable, in view of altered spacial conditions, to expect this expression to hold rigorously for liquids; on the other hand there are sufficient grounds to believe that it will hold approximately. First, other things being equal, collision frequency is proportional to the product of molecular densities, as has been stated in the classical view of bimolecular reaction rates. Second, it is proportional to the molecular velocity, which is proportional to  $\sqrt{T}$ . Finally the other variables,  $m_1$  and  $\sigma_1$ , tend to vary within small limits, and further as the temperature increases  $\left(\frac{m_1+m_2}{m_1m_2}\right)^{\frac{1}{2}}$  increases while  $\left(\frac{\sigma_1+\sigma_2}{2}\right)^2$  decreases, since the mass and size of the complexes may be safely assumed to decrease somewhat

G. W. Stewart and collaborators, Physic. Rev., 35, 726, 1929; 38, 1575, 1931.
 H. Jeans, Dynamical Theory of Gases, 4th ed., cf. p. 251.

with increased temperature (cf. Stewart). Thus it may be postulated that, as a first approximation, the collision frequency can be represented by  $KN_1N_2\sqrt{T}$ , where K is a proportionality constant that includes all other constants. Applying this to the definition of t,

$$t = \frac{N_1}{KN_1N_2\sqrt{T}} \qquad . \qquad . \qquad . \qquad (6)$$

Cancelling out  $N_1$ , and using the Boltzman distribution to determine  $N_2$ ,

$$t = \frac{1}{KA_2 \frac{\rho}{m_0} e^{-Q/RT} \sqrt{T}} . \qquad (7)$$

where  $A_2$  is the distribution constant,  $\rho$  the density, and Q the mean energy of dissociation of the groups. Combining all constants and calling its reciprocal K', and substituting  $\rho = 1/V$  where V is the volume, equation (7) simplifies to,

$$t = \frac{K'V}{\sqrt{T}} e^{Q/RT} . . . . (8)$$

2. The elasticity (or shear) modulus of equation (2) may be evaluated by relating it to the bulk modulus B. E is defined as the ratio of the stress P to the strain  $\Delta l/l$ ,  $\Delta l$  being the linear displacement along the length l, and l as the ratio of the stress l to the strain l0, l1, l2 being the volume change of the original volume l2. The two can be connected in a fashion similar to linear and cubic expansion. Assuming

$$(V + \Delta V) = \frac{4\pi}{3}(l + \Delta l)^3 = \frac{4\pi}{3}(l^3 + 3l^2\Delta l + 3l\Delta l^2 + \Delta l^3)$$

and subtracting V which equals  $\frac{4\pi l^3}{3}$ , one obtains

$$\Delta V = \frac{4\pi}{3} (3l^2 \Delta l + 3l \Delta l^2 + \Delta l^3).$$

Neglecting second order delta's, and substituting in the expression for B,

$$B = \frac{P}{\frac{\Delta V}{V}} = \frac{P}{\frac{4\pi}{3}3l^2\Delta l} = \frac{P}{\frac{3\Delta l}{l}}.$$

Therefore,

$$E = 3B$$
 . . . (9)

Or, as the bulk modulus is the reciprocal of the compressibility

$$\beta = \left(\frac{\partial V}{\partial P}\right)_{\mathbf{T}} \frac{\mathbf{I}}{V},$$

$$E = \frac{3}{\beta} \quad . \qquad . \qquad . \qquad . \qquad (10)$$

Using (3), the equation in the liquid state for elasticity in terms of compressibility is,

$$\beta = \frac{3}{A_1}e^{CT} \qquad . \qquad . \qquad . \tag{11}$$

3. The final evaluation of Maxwell's equation is obtained simply by substituting equations (8) and (10) in (2), and designating 3K' by K'',

$$\eta = \frac{K''V}{\beta\sqrt{T}}e^{Q/RT} \qquad . \tag{12}$$

An alternative expression results if the value of  $\beta$  found in (11) is used, and  $A_1K$  designated by K''':

$$\eta = \frac{K'''V}{\sqrt{T}}e^{\frac{Q}{RT} - CT} \qquad . \tag{13}$$

The similarity to the "thermodynamic" equation (I) will be readily observed.

# II. Viscosity Under Pressure.

The application of an external field to a liquid will, as M. P. J. Iyer <sup>11</sup> has observed, alter the ratio of the types of molecules, and if the external field is that of high pressure alter the volume. It may be added that the elastic properties, *i.e.*, the compressibility, will be changed also. These changes can be represented in equation (12), which as it stands does not show the shift in the types of molecules. The latter depends upon the effect of the field on the potential energy of the molecules. If the additional potential is proportional to the field, the dissociating molecules have to work against their original dissociation energy plus the potential from the field, and (12) then becomes,

$$\eta_{\rm P} = K'' \frac{V_{\rm P}}{\beta_{\rm P} \sqrt{T}} e^{\left(\frac{Q + \alpha Q_{\rm f}}{RT}\right)} \qquad . \tag{14}$$

where  $\alpha$  is a proportionality constant,  $Q_f$ , the potential of the field, and the subscripts p denote properties at pressure P. If  $Q_f$  may be expressed by  $P\Delta V$  where P is the pressure causing the change in volume  $\Delta V$ , (14) becomes,

$$\eta_{\rm P} = K'' \frac{V_{\rm P}}{\beta_{\rm P} \sqrt{T}} e^{\left(\frac{Q + \alpha P \Delta V}{RT}\right)} \qquad . \tag{15}$$

At constant temperature the ratio of the viscosity at pressure to the ordinary atmospheric viscosity is

$$\frac{\eta_P}{\eta_0} = \frac{V_P}{\beta_P} \cdot \frac{\beta_0}{V_0} e^{\frac{\alpha P \Delta V}{RT}} \qquad (16)$$

where the zero subscripts  $_0$  denote properties at atmospheric pressure. The only unknown in equation (16) is the proportionality constant  $\alpha$ .

Other high pressure equations for viscosity, save the volume functions which fail, are a three-constant semi-empirical formula of Lederer, <sup>12</sup> and a three-constant equation of Andrade, mentioned by Bridgman <sup>13</sup> but not derived.

#### III. Verification of Equations.

It is possible to represent equations (11), (12) and (16) graphically each in a logarithmic form, as shown in Figs. 1, 2 and 3.

M. P. J. Iyer, loc. cit., 6.
 E. L. Lederer, loc. cit., 6.
 P. W. Bridgman, Physics of High Pressure, p. 356.

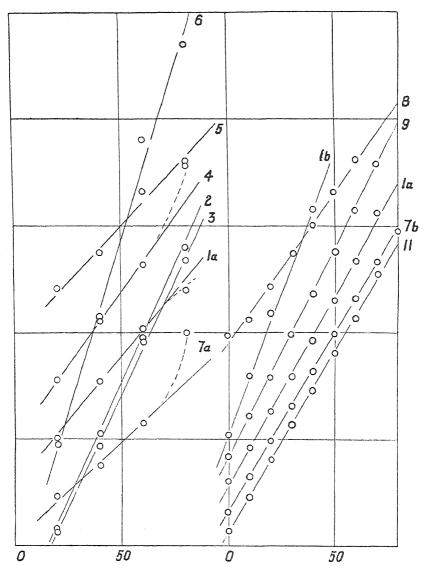


Fig. 1.—Plot of T (abscissa) against  $\log \beta$  (ordinate). The lines on the left are from Bridgman's data, on the right from Tyrer's data. The co-ordinates of Log  $\beta$  have been shifted to prevent overlapping of lines.

# Substances :--

- 1a. Methyl alcohol, Bridgman.
- 1b. Methyl alcohol, Tyrer.
- 2. Ethyl alcohol.
- 3. Propyl alcohol.
- 4. Isobutyl alcohol.
- 5. Amyl alcohol.6. Carbon disulphide.
- 7a. Ethyl iodide, Bridgman.
- 7b. Ethyl iodide, Tyrer.
- 8. Acetic acid.
- 9. Ethyl acetate.
- 10. Carbon tetrachloride.
- 11. Benzene. 12. Water.
- 13. Ether.
- 14. Acetone.

Equation (11) holds fairly well for some liquids and only approximately for others. The discrepancy might be due to the experimental figures, since the equation is followed by the data of some investigators and not

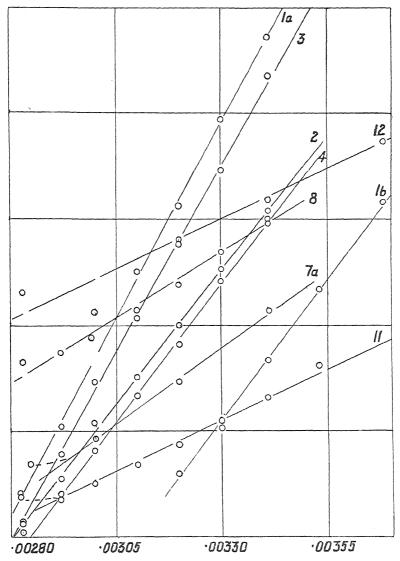


Fig. 2.—Plot of  $\frac{\mathbf{I}}{T}$  (abscissa) against Log  $\frac{\eta\beta\sqrt{T}}{V}$  (ordinate). The co-ordinates of Log  $\frac{\eta\beta\sqrt{T}}{V}$  have been altered to keep all substances on the graph. See note to numbers on Fig. 1.

others. Water is known to be anomalous, decreasing in compressibility to a minimum around  $60^{\circ}.$ 

Equations (12) and (16) give good agreement considering experimental

data. The viscosity of water at high pressure is quite different from all liquids, decreasing with pressure to a minimum around 1000 kg. in the

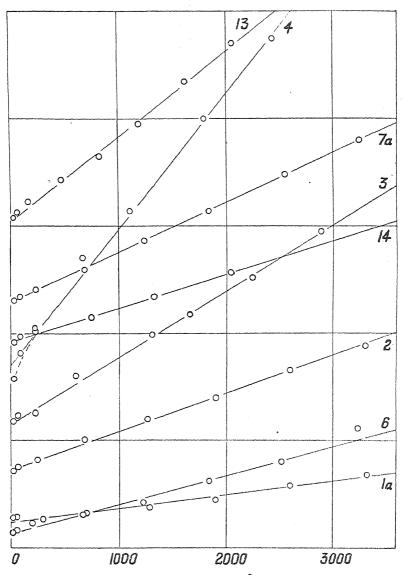


Fig. 3.—Plot of  $P\Delta V$  (abscissa) against Log  $\frac{\eta_P\beta_P}{\eta_0V_P}$  (ordinate), at 30°. The coordinates of Log  $\frac{\eta_P\beta_P}{\eta_0V_P}$  have been moved up regularly for each substance. The  $P\Delta V$  co-ordinate of Ether has been halved. See note to numbers on Fig. 1.

lower temperature range. If water is considered to contain an equilibrium of *simple* molecules of di- and tri-hydrol at low temperatures, an application of pressure will favour the formation of di-hydrol, since the tri-hydrol

(ice) happens to be of larger volume. Should the energy of dissociation of complexes of the di-hydrol be less than that of tri-hydrol, when the equilibrium is shifted by pressure towards di-hydrol, then the mean energy of dissociation Q will be less than before. This effect is greater than the increase in potential of the field at lower pressures, which accounts qualitatively for the minimum in viscosity.

The constants in equation (13) may be calculated accurately from three simultaneous equations in exponential form. Table I. shows Q to

TABLE I.

	Q in Cals. per Mol.	$C \times 10^5$ .	K'''.	α*.
Methyl alcohol . Ethyl alcohol . Propyl alcohol . Ethyl formate . Ethyl acetate . Acetone . Ethyl iodide . Chloroform . Carbon disulphide Benzene	1095·9 1961·0 3598·3 1728·8 1865·6 1064·3 1111·6 708·48 577·40 2235·4 1713·3	703·05 689·28 332·70 16·075 56·630 354·10 271·25 531·80 367·85 71·162	•11883 •041676 •0016892 •0034763 •0033567 •020141 •063007 •20116 •086328 •0025495 •0049972	·095 ·23 ·41 ———————————————————————————————————

be of the right order of magnitude. It may be mentioned that C for water is positive, which would be expected if  $\beta$  decreases with the temperature. The constants may then be reintroduced into (13) and the viscosity calculated. Table II. illustrates the agreement for a number of representative

The relaxation time t may be calculated directly by substitution of (10) in (2). Table III. illustrates the order of t, and its variation with the

temperature for a few substances. It is to be noted that this is of a smaller order than Debye's relaxation time. This discrepancy arises from a difference in definition of terms. Debye's 14 term is defined as "the time required for moments to revert to a random distribution after removal of an impressed field," whereas in this investigation t is taken as the time of relaxation of elastic force, or the time a body sustains a stress. Since the former is related

TABLE III.

T.	t × 10 <sup>13</sup> .	t × 10 <sup>13</sup> .
	Ethyl Alcohol.	Propyl Alcohol.
20	4.13	6.95
40	3.81	4.77
60	2.54	3.47
80	1.21	2.58
	Ethyl Iodide.	Acetone.
20	2.10	1.29
40	1·80	1.24
60	1.59	
	-	

to the interval between collisions, it is expected to be of larger order than t, which is connected to the interval during a collision.

The viscosity data were obtained from Thorpe and Rodger, 15 Lederer, 16 and the International Critical Tables; 17 the volume data from Batchinski, 4

re-volume was taken in kilogram-centimetre units.

1. r. Debye, Polar Molecules, p. 83.

<sup>&</sup>lt;sup>15</sup> T. E. Thorpe and J. W. Rodger, Phil. Trans., 185A, 397, 1894; 189, 71, 1897.

16 E. L. Lederer, loc. cit., 6.

<sup>17</sup> International Critical Tables, Vol. V., p. 12; VII., 213 ff.

TABLE II.

								***********	
т.	η Experi- mental × 10 <sup>5</sup> .	$^{\eta}_{\text{Cal-}}$ culated $^{\text{ro}^5}$ .	Per Cent. Diff.	Experimental × 105.	n Cal- culated 10 <sup>5</sup> .	Per Cent. Diff.	Experi- mental × 105.	Cal- culated 10 <sup>5</sup> .	Per Cent. Diff.
	Methy	l Alcohol		Et	hyl Alcoho	ol.	Pro	pyl Alcoh	ol.
0	808	790.2	2.20	1770	1777.0	0.40	3882	3862	0.21
IO	686	681.3	0.68	1449	1448.4	0.04	2917	2934	0.24
20	591	591.0	0.00	1192	1192.0	0.00	2255	2255	0.00
30	515 451	515·2 451·0	0.04	990 828	989·2 828·2	0.08	1777 1403	1767 1403	0.20
40 50	396	396.6	0.15	698	695.5	0.36	1128	1129	0.09
60	350	350.0	0.00	592	592.0	0.00	919	919.0	0.00
70				505	507.8	0.55	757	757:3	0.04
80	-	_					628	628.3	0.05
	1	1	1			<u> </u>		!	<u> </u>
		Formate.		B .	hyl Aceta			A cetone.	
0	505	504.2	0.16	578	579·1	0.10	399	403.7	0.00
10 20	448	448.0	0.00	507 449	507·5 449·0	0.00	362 325	362·0 326·5	0.46
30	362	361.7	0.10	401	400.5	0.13	296	296.0	0.00
40	328	329.0	0.33	360	360.0	0.00	271	269.7	0.48
50	300	301.3	0.43	326	325.9	0.03	246	246.6	0.24
60	-	_		297	297.0	0.00	_		
70				270	272.3	0.85			-
	Ethy	l Iodide.			Chloroform	•		Benzene.	
0	719	716.9	0.20	700	692.8	1.03	900	874.0	12.88
10	645	644.7	0.05	626	623.8	0.35	746	744.4	0.21
20	583	583.0	0.00	564	564.0	0.00	642	642.0	0.00
30	530	530.0	0.00	511	512.0	0.50	561	558.9	0.37
40 50	484	484.0	0.00	466	466.0	0.00	492	491.0	0.20
60	444	444.0	0.00	426 390	425·7 390·0	0.07	436 389	434.9 388.0	0.26
70	378	378-2	0.05	J9-	350		350	348.6	0.40
80	-	-	-				317	314.8	0.69
	1	1	1		1	1		}	}
		Octane.			on Disulp				
0	706.0	699.2	0.96	430	430.0	0.00			
10 20	541.9	612·9 541·8	0.49	396	396.6	0.14			
30	482.8	482.6	0.02	367 342	367·0 340·7	0.38			
40	432.8	433.8	0.23	319	317.4	0.50			
50	390.7	390.7	0.00						
60	355.1	354.7	0.11						
70 80	324.1	323.8	0.00						
90	273.0	297.1	0.00						
100	252.0	253.6	0.63						
	1	1	1		1	1			

Bridgman, 18 and International Critical Tables 19; the high pressure data from Bridgman 20; and the compressibility data from Bridgman 18 and Tyrer. 21

I am particularly indebted to Dr. Mouquin under whose direction this investigation was carried out, and to Mr. Spector and Dr. West, who have helped me immeasurably.

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#### THE SYSTEM: MANGANESE-TIN-MERCURY.

By Alan Newton Campbell and Herbert Dyson Carter.

Received 21st September, 1933.

In phase rule work it is customary to study the solubility isotherms of salt pairs in water at different temperatures, with a view to determining the transition temperature of the double salt, if one exists; the fusion curve of the mixed salts is by itself incapable of yielding this information. It seems that a similar method of investigation may be applicable to the intermetallic compounds formed in alloys, using mercury as solvent. The results, plotted on triangular co-ordinates with a vertical temperature axis should yield exactly similar information to the investigation of salt-pairs in water. It is, of course, very probable that compound formation between the components or the compound and mercury may take place, just as single or double salts may be hydrated. It is not supposed, however, in the case of hydration, that this has any appreciable effect on the range of stability of the double salt, nor should compound formation with mercury, a process associated with a smaller energy change, have any effect. The formation of solid solutions is also possible, but, unless the series of solid solutions is continuous, the curves should still be susceptible of interpretation.

It was decided to test these ideas on the hitherto unstudied system, manganese-tin. Tin is said to have a large solubility in mercury.<sup>2</sup> It has also been shown by one of us <sup>3</sup> that amalgams of manganese can readily be produced electrolytically, with separation of a solid phase.

#### Experimental.

Although our experiments were eventually successful, considerable difficulty was met with at the start and the technique had continually to be refined. In view of the importance of a new method of metallurgical study, the technique is dealt with in detail.

The mercury used was originally purified by treatment with dilute nitric acid, but it was not distilled. The manganese sulphate and ammonium sulphate used in the electrolytic formation of manganese amalgams were ordinary C.P. chemicals; traces of impurity, such as iron, do not affect the electrodeposition of manganese in mercury, because of the high overvoltage at a mercury surface, although they do affect, or entirely inhibit, its deposition on a solid cathode. The tin used was commercial tin. This was completely analysed and found to contain 99.7 per cent. tin.

Establishment of Equilibrium.—The electrolytic cell for the production of manganese amalgams \* was immersed in a thermostat. The mercury cathode was well stirred mechanically. Using a manganese sulphate-ammonium sulphate electrolyte, and pure mercury only as cathode, and conducting electrolyses for increasing periods of time, the figures in Table I. were obtained for the manganese content of liquid amalgams. It appears from this that saturation is attained after forty minutes electrolysis and the constancy of the manganese content also shows that

<sup>3</sup> J.C.S., 125, 1713, 1924.

<sup>&</sup>lt;sup>1</sup> Cf. Campbell, Nature, 131, 438, 1933.

<sup>&</sup>lt;sup>2</sup> Mellor, Comprehensive Treatise on Inorganic Chemistry, Vol. VII., p. 376.

the solid phase separating is pure manganese and not a solid solution of mercury in manganese.

For the preparation of tin-mercury amalgams, an amalgam rich in tin was first produced by pouring molten tin into mercury in an atmo-

TABLE I .- TEMPERATURE 30.0°.

Durati	on of Run.	Manganese in Liquid Phase
5 n	ninutes	o o 15 per cent.
10	,,	0.030 ,,
15		0.055 ,,
20	• •	0.070 ,,
30	,,	0.100 ,,
40	,,	0.120 ,,
60	,,	0.115 ,,
75	"	0.122 ,,
90	"	0.120 ,,
120	**	0.122 ,,

sphere of carbon dioxide and subsequently stirring in the thermostat for twenty-four hours. The liquid amalgam was filtered off and this could be diluted with mercury to any desired extent. At first, the practice was to use one of these diluted tin amalgams as cathode and plate in manganese up to saturation. This was found to be not very satisfactory, since duplicate tests did not

yield duplicate figures. The method can be made satisfactory if prolonged stirring is carried on after plating is finished. That equilibrium is not immediately attained is to be attributed to the high viscosity, almost amounting to rigidity, of these amalgams, which makes mechanical stirring very ineffectual.

The technique was now varied, so that saturated tin and manganese amalgams were separately prepared, mixed in suitable proportions, and stirred in the thermostat, with appropriate solid phase, for six hours. This method was used for the 30° isothermal.

Finally, the above method of mixing tin and manganese amalgams in appropriate proportions was retained, but the amalgams were mixed in stoppered bottles attached to a rotating wheel in the thermostat. The mixture is thus inverted once in every revolution and with these heavy, viscous liquids this is much more effectual than any mechanical method of stirring. This method was used for the 55° and 70° isothermals.

Filtration of Liquid Amalgam from Solid Phase.—Richards, Wilson and Garrod-Thomas have shown that ordinary methods of filtration result in the passage of solid phase along with the liquid amalgam. Indeed, very few workers have attempted to separate the solid phase from the amalgam, and hence most so-called solubility measurements in mercury are worthless. For example, the true solubility of copper in mercury is only 0.002 per cent., whereas much greater solubility was reported by earlier workers. In this work, filtration was carried out actually in the thermostat, as it always should be when the analysis of the solid phase is of importance. After trying various filtration media, chamois leather was found to be the most satisfactory, not only because it is a perfect filtration medium for the purpose, but because it can readily be cleaned. The filtration apparatus consisted of a glass tube over the end of which the chamois was strapped. Pressure was applied above the amalgam, by means of compressed air. The solid phase remained as a conveniently handled pellet, in the tube.

Methods of Analysis.—Considerable difficulty was met with in getting the dissolved metals into solution. The method used for the 30° and 70° isothermals was to boil the weighed sample with concentrated hydrochloric acid for six hours, adding acid from time to time. When vigorous action ceased, and the acid boiled with large bubbles, five drops of nitric acid, for each 100 c.c. of hydrochloric acid, were added. Vigorous action started again, and the tin and manganese were found to have dissolved completely after a further one hour's boiling. Tin was determined by reduction with aluminium powder in an atmosphere of carbon dioxide,

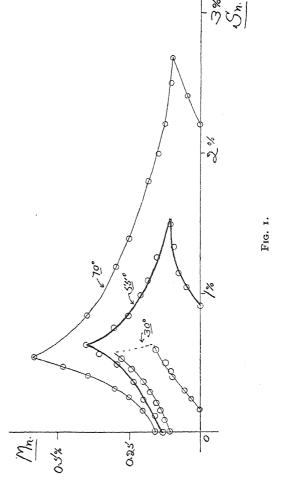
followed by iodine titration. Manganese was determined on a separate portion by addition of sulphuric acid, evaporation to the fuming state, dilution, neutralisation, and titration with permanganate (Volhard's method).

For the 50° isothermal, a more convenient method of procuring solution of the dissolved metals was devised, based on the work of Russell.<sup>5</sup> A

weighed portion of the amalgam was shaken with permanganate of known strength presence of sulphuric acid, using 20 c.c. at a time, until the endpoint was attained, i.e., until all metals except mercury were in solu-The end-point tion. is indicated by a tendency of the mercury to break into globules or fine dust. The total permanganate represents the amount required to oxidise both tin and manganese. According to Russell, no mercury passes into solution till all the other metals are out. The tin in the solution was then determined as above, and the manganese obtained by difference from the permanganate titration. This method is extremely accurate if sufficiently dilute permanganate is used. It is, however, laborious unless a mechanical shaker is used. Vigorous shaking is essential to prevent mercury passing into solution (Russell).

The mercury used in preparing the amalgams was cleaned by

the permanganate method and used again.



Solubility Measurements.—According to Pushin 6 tin forms no definite compound with mercury. The main point of investigation was whether or not manganese and tin form a compound at room temperature, or in the neighbourhood of room temperature. Table II. contains the results of the solubility determinations.

In Fig. 1, the results for the liquid phases are plotted on rectangular co-ordinates. The curves are exactly of the type obtained with two salts

<sup>&</sup>lt;sup>5</sup> Russell, Cazalet and Irvine, *J.C.S.*, 841 *et seq.*, 1932. <sup>6</sup> *Z. anorg. Chem.*, **36**, 201, 1903.

TABLE II.

Liquid	Phase.	Solid	Phase.
Mn.	Sn.	Mn.	Sn.
	30° Isotl	nermal.	alting with gold Ecological Programming and Programming and Programming States of Municipal research Affronce Peterline
o·12 per cent.	o·oo per cent.	2.0 per cent.	oo per cent.
0.12 ,,	0.08 ,,	0.6 ,,	8.1 ,,
0.14 "	0.16 ,,	0.9 ,,	6.8 ,,
0.16 "	0.50 ,,	0.3 ,,	7.5 "
0.18 ,,	0.28 ,,	1.5 ,,	7.7 ,,
0.20 ,,	0.35 ,,	1.9 ,,	7.7 "
0·24 ,, 0·27 ,,	0.45 ,,	2.0 ,,	6.7 ,,
0100	0.17	2.7 ,,	1 0.0
0.03 ,,	0.23 "	0.0 ,,	2.2 ,,
0.06 ,,	0.30 "	7.3 ,,	0.3 ,,
0.09 ,,	0.41 ,,	73 "	J ",
O·II ,,	0.44 ,,	2.0 ,,	1.6 ,,
0.13 ,,	0.50 ,,	6.0 ,,	1.3 "
0.16 "	0.59 ,,	0.6 ,,	1.5 ,,
	55° Isoth	ermal.	
o·oo per cent.	o-90 per cent.	(Figures for in	itermediate part
0.05 ,,	0.06 ,,	of curve only	
0.07 ,,	1.15 ,,	1 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3 3	7
0.09 ,,	1.34 ,,		
0.10 "	1.50 ,,		
0.13 "	0.00 ,,		
0.16 ,,	0.12 ,,		
0.20 ,,	0.23 ,,		
0.30 "	0·35 ,, 0·48 ,,		
0.36 ,,	0.55		
0.40 ,,	0.62 ,,		
0.30 ,,	0.75 ,,	o·73 per cent.	o.44 per cent
0.25 ,,	0.83 ,,		
0.22 ,,	0.98 ,,	0.55 ,,	0.50 ,,
0.18 "	1.10 "		
0.16 "	1.27 ,,	0.52 ,,	0.55 ,,
	70° Isotl	iermal.	
o·oo per cent.	2.2 per cent.	0.00 per cent.	1 9.7 p.c.
0.10 "	2.7 ,,	0.14 ,,	13.4 ,, >Sn
0.05 ,,	2.4 ,,	No-Marie	branc
0.58 ,,	0.67 ,,		]
0·15 ,, 0·20 ,,	2·00 ,, 1·80	1.8	14.3 "
0.13 "	2.50	1.5 ,,	II.o " Inter-
0.25 ,,	7140	I·I ,, 2·0	9.5 " >media
0.300 ,,	1.20	212	branel
0.40 ,,	0·85 ,,	3.0	10.5 "
0.14 ,,	2.20 ,,	3'2 ",	14.0 ,,
0.16 ,,	0.00 ,,	6.3 "	0.00
0.20 ,,	0.15 ,,	11.3 ,,	0.17 ,,
0.25 ,,	0.27 ,,	8.6 ,,	0.45 , Mn
0.31 ,,	0.40 ,,	-	- branch
0·40 ,, 0·48 ,,	0·50 ,, 0·70 ,,	9·I ,,	0.90 ,,
	0.70 ,,		

(having a common ion) and water, where double salt formation takes place. The intermediate portion of the 30° isothermal is hypothetical: it could not be realised experimentally, partly because its range is small, but principally because at 30° all solubilities in mercury are small and the experimental error proportionately great. It was for this reason that work at higher temperatures was undertaken, since it had been observed that the solubility both of tin and of manganese increased considerably at higher temperatures. The form of the curves shows that a compound is formed between tin and manganese and that the transition temperature is approached by lowering the temperature. The compound is therefore endothermic. The transition temperature appears to lie only very slightly below 30°, if, indeed, the compound exists at that temperature.

In order to evaluate, if possible, the formula of the compound, the

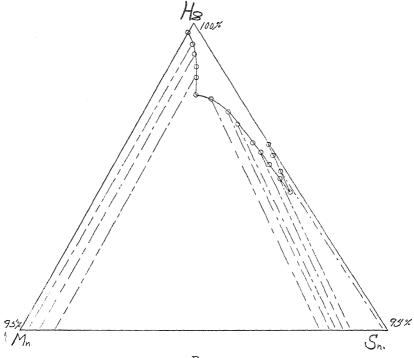


FIG. 2.

figures for liquid and solid phases, at  $70^{\circ}$ , were plotted on a triangular diagram (Fig. 2). [Owing to the high mercury content even of the solid phases, the diagram had to be drawn on a very large scale, and therefore only the top portion of the diagram is reproduced here.] The tie-lines from the intermediate branch intersect on the base line, indicating a definite compound, uncombined with mercury. The point of intersection corresponds to a composition of 85 per cent. tin, 15 per cent. manganese, agreeing with an empirical formula of  $Sn_5Mn_2$ . The tie-lines from the tin and manganese branches intersect approximately at the angular points; exact coincidence is hardly to be expected.

The above compound was isolated by heating a mixture of manganese and tin amalgams in water, at from 50° to 100°. After some time, flakes of insoluble solid were removed. The composition of this solid was determined by Russell's method, *i.e.*, it was shaken with permanganate

and sulphuric acid till excess metal was removed. The volume of permanganate required to remove both metals together was then noted and the tin determined in the extract. The formula given by Russell, adapted to the case of manganese and tin, was then applied. This gave the composition as: 87 per cent. tin, 13 per cent. manganese, corresponding to Sn<sub>3</sub>Mn.

#### Discussion.

The results of this paper show that it is possible to study systems of two metals in mercury, in a manner precisely analogous to the study of two salts and water. The case studied happens to be very simple in that neither the components nor the compound form solid solutions with the mercury. It may be that we exaggerate the possibility of this happening and that there is but little tendency for metals and metallic compounds to separate from liquid solutions in mercury with dissolved mercury in them. If so, the applicability of the method is all the greater.

The technique of the method is not conspicuously easy, but it

presents no insuperable difficulties.

It appears that manganese and tin form a compound, stable above 30°, which has the formula  $Sn_5Mn_2$  or  $Sn_3Mn$ . We prefer the former formula, because we consider the method described here to rest on surer theoretical foundations than that of Russell.

#### Abstract.

- I. It is shown that it is possible to study systems consisting of two metals and mercury, in a manner precisely analogous to the study of two salts and water. This means that exact information can be obtained as to the mutual relationships, compound formation, etc., of two metals at temperatures in the neighbourhood of room temperature.
  - 2. The system: manganese-tin-mercury has been studied.
- 3. A compound, having the formula  $\mathrm{Sn}_5\mathrm{Mn}_2$  is shown to exist, having a transition temperature in the neighbourhood of room temperature.
- 4. Neither the components not the compound form solid solutions with mercury, nor do they form compounds analogous to hydrates.

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# THE TEMPERATURE COEFFICIENT OF THE DECOMPOSITION OF HYDROGEN PEROXIDE IN THE PRESENCE OF POTASSIUM IODIDE.

By WILLIAM C. K. HENDER AND ROBERT A. ROBINSON.

Received 18th October, 1933.

The collision theory of chemical reaction has been remarkably successful in recent years in explaining the mechanism of reactions in the gaseous phase, but few attempts have been made to extend the theory to reactions in solutions. Norrish and Smith  $^1$  measured the velocity of reaction between trimethylamine and m- and p-nitrobenzyl chloride in

non-polar solvents and found that collisions between two reacting molecules would not account for the observed temperature coefficient and that it was probable that the solvent molecules played an essential part in the reaction. More recently Moelwyn-Hughes and Legard  $^2$  have been successful in accounting for the reaction between iodine and  $\beta$ -phenylpropiolic acid in aqueous solution on the basis of three-body collisions between the reacting substances and the solvent. Their success is particularly encouraging in that the theoretical treatment seems to be applicable to reaction between charged particles in a polar medium.

We have investigated the temperature coefficient of the decomposition of hydrogen peroxide with potassium iodide as catalyst, studying the effect of concentration of catalyst, the presence of neutral salts and the nature of the solvent medium. One determination of the temperature coefficient has been made previously by Walton, while Harned and French have studied the neutral salt effect at 25°.

# Experimental.

Reaction velocities were measured in carefully controlled thermostats at 15°, 25°, 30°, 35° and 45° either by titrating the solution at intervals or by measuring the volume of oxygen evolved during the reaction. The former method  $^6$  was used for low reaction rates (k < o·o·15) and the gas-volumetric method for the higher rates. As supersaturation of the solution with oxygen appears to retard the reaction, the solution was stirred at a speed of at least 750 r.p.m.

All reagents were of the purest quality. Hydrogen peroxide was distilled from Merck's product and the neutral salts were of A.R. grade. The method of Guggenheim 7 was used for calculating the velocity constants in the gas-volumetric experiments. These constants are expressed

in gram mols. per litre and minutes as units.

Table I. gives the observed velocity constants with varying concentrations of catalyst in aqueous solution, together with the values of k/[KI], i.e., the velocity constant at unit concentration of the catalyst. From the latter the values of  $k_{T+10}/k_T$  for three temperature intervals are obtained and thence the value of the energy of activation from the Arrhenius equation. For this Walton obtained a value of 13,630 cal.

[KI].	o or N.	0°02 N.	0°04 N.	o•o6 N.	Mean k/[KI].	$k_{\mathrm{T+10}}/k_{\mathrm{T}}.$	E.	
$egin{array}{c} k_{15} \\ k_{25} \\ k_{35} \\ k_{45} \end{array}$	0.00592 0.01347 0.02845 0.0570	0.01206 0.02691 0.05690 0.1161	0.02356 0.05428 0.1149 0.2325	o·o3583 — —				
$k_{15}/[{ m KI}] \ k_{25}/[{ m KI}] \ k_{35}/[{ m KI}] \ k_{45}/[{ m KI}]$	0·592 1·347 2·845 5·700	0.603 1.346 2.845 5.805	0·589 1·357 2·873 5·813	o·597 — — —	0·596 1·350 2·854 5·773	2·265 2·114 2·023	13,945 13,640 13,700	

TABLE I.—Effect of Catalyst Concentration.

Mean E = 13,760 cal.

 <sup>&</sup>lt;sup>2</sup> J. Chem. Soc., 424, 1933.
 <sup>4</sup> J. Amer. Chem. Soc., 40, 1461, 1918.
 <sup>5</sup> J. physical. Chem., 32, 401, 1928.
 <sup>6</sup> Titrations were performed as recommended by Kolthoff, Z. anal. Chem.,

<sup>60, 400, 1921.

&</sup>lt;sup>7</sup> Phil. Mag., 2, 538, 1926.

Table II. gives the velocity constants at four temperatures in the presence of various neutral salts and 0.02 N potassium iodide. The energy of activation, E, was obtained from the slope of the plot of  $\log k$  against  $\mathbf{I}/T$ .

Salt.	k <sub>15</sub> .	k <sub>25</sub> .	k <sub>35</sub> .	k45.	E.	E'.
1 N-NaCl 1 N-KBr 1 N-K <sub>2</sub> SO <sub>4</sub> . 1 N-MgSO <sub>4</sub> . 0.5 N-BaCl <sub>2</sub> . 1 N-BaCl <sub>2</sub> .	. 0.01453 . 0.01341 . 0.01065 . 0.01580 . 0.01771 . 0.02559	0.03197 0.02930 0.0249 0.03570 0.04010 0.05320	0.06709 0.06370 0.05153 0.07421 0.0881 0.1183	0·1387 0·1304 0·1096 0·1532 0·1805 0·2369	13,750 13,790 13,990 13,770 14,080 13,990	17,490 17,410 17,740 18,060 17,810

TABLE II.—EFFECT OF NEUTRAL SALTS.

Finally Table III. shows the effect of a change in the solvent medium, the solvents used being either pure liquids or aqueous mixtures. In the former case, the solvents were dried in the ordinary way, but no precautions were taken to ensure complete drying since the decomposition of the peroxide produced water to the extent of about 0.2 per cent., and moreover, water was supplied to the solution by the introduction of hydrogen peroxide in the form of a concentrated solution. In practice, the solutions contained about 0.4 per cent. of water. Good unimolecular constants were obtained, so that it is improbable that the slight change in the nature of the solvent had any appreciable effect.

Medium.			k <sub>15</sub> .	k <sub>25</sub> .	k30.	k <sub>35</sub> .	k45.	E.
25·5 p 54·4 87·8 100 54·4	er cen	at. $CH_3OH$ . $C_2H_4'(OH)_2$	0.00641 0.00336 0.00235 0.00195 0.00382 0.00460 0.0146	0.0145 0.00848 0.00611 0.00531 0.00985 0.0132 0.0352	0·00841 0·0220 0·0513	0.0331 0.0196 0.0150 0.0132 0.0238 0.0337 0.0747	0.0717 0.0454 0.0358 — 0.0569	15,080 15,790 16,550 16,810 16,380 17,790 14,300

TABLE III.—EFFECT OF CHANGE IN THE SOLVENT MEDIUM.

In all cases the catalyst was 0.02 N potassium iodide. The percentages given in Table III. are weight percentages. The data given in the table for ethylene glycol as solvent are not of a high order of accuracy but they are included here because of the interest which attaches to a highly viscous solvent. The only work using non-aqueous solvents appears to be that of Bohnson  $^8$  who has measured the reaction velocity in aqueous solutions of alcohols, glycerine and pyridine but only at  $^25^\circ$ . Our results agree with his in so far as they can be compared.

#### Discussion.

In no case have we obtained any indication that the reaction is other than unimolecular with respect to hydrogen peroxide. Moreover, Table I. shows that the rate is directly proportional to the iodide concentration, so that the reaction occurs between single molecules and ions of peroxide and iodide. Calculation shows that in these concentrations the velocity is not proportional to the activity of the potassium iodide.

The assumption that reaction occurs on collision between peroxide molecules and iodide ions having a joint energy, E, in excess of the normal energy leads to a value of the velocity constant given by:

$$k = \frac{N_0}{1000} \cdot \pi \sigma^2 \sqrt{\mu_1^2 + \mu_2^2} e^{-E/RT},$$

where  $N_0$  = number of molecules per litre =  $6.06 \times 10^{23}$ .

 $\sigma$  = mean diameter of the molecules,

 $\mu_1, \mu_2$  = root-mean-square velocities of the molecules.

The latter can be calculated from the equation 9:

$$\mu = 14,500\sqrt{T/M}$$
 cm. per. sec.

where M is the molecular weight. Using a value of  $\sigma = 5 \times 10^{-8}$  cm. the calculated velocity constant at 25° is 18, whereas the observed constant is 0.026 with seconds as the unit of time. If, however, we assume that a triple collision associated with energy E', between peroxide, iodide and water is necessary for reaction, the formula developed by Moelwyn-Hughes and Legard 10 can be employed, namely:

$$k = \frac{N_0}{1000} \frac{3\pi\eta\sigma}{2m_A n_W} e^{-E'/RT},$$

where  $\eta = \text{viscosity of the solution} = 9 \times 10^{-3} \text{ g./cm. sec.}$ 

 $n_{\mathbf{W}}$  = number of solvent molecules per c.c.

 $= 3.37 \times 10^{22}$ 

 $m_{\rm A} = {\rm mass~of~iodide~ion} = 2.09 \times 10^{-22}$ 

and E', the modified energy of activation defined by

$$d/dT \log_e k/\eta = E'/RT.^2$$

is 17,710 Cal. This leads to the following values of k.

Temp.	15°.	25°.	35°∙	45°•
k (calc.)	0.0082	0.018	0.039	0.079
k (obs.)	0.010	0.023	0.048	0.083

The satisfactory agreement supports the hypothesis that the solvent is participating in the effective collisions which result in reaction.

Rice and Kilpatrick 11 have measured the velocity of reaction between iodine and acetone in acid solutions and found that the temperature coefficient of the reaction is independent of the presence of non-electrolytes such as sucrose, methyl alcohol, etc. The decomposition of hydrogen peroxide appears to proceed with the same energy of activation in the presence of neutral salts, the mean value of the data given in Table II. after the viscosity correction is made being 17,660 Cal., i.e., practically that found in the absence of neutral salts and the average deviation from the mean is less than I per cent., if the result in the case of magnesium sulphate be omitted on account of the lack of reliable viscosity figures for these solutions. From the above equation, the salt effect may be considered to be due to (I) a change in the viscosity of the solution, (2) a diminution in the number of solvent molecules per c.c., and (3) a small change in E' caused by interionic forces. These effects are small in comparison with the assumptions made in deducing

<sup>&</sup>lt;sup>9</sup> Tolman, "Statistical Mechanics," 63, 1927.

10 Vide also Jowett, Phil. Mag., 8, 1059, 1929.

<sup>&</sup>lt;sup>11</sup> J. Amer. Čhem. Soc., **45**, 1401, 1923.

the number of three-body collisions, and computation from the equation is, therefore, of little value. The results are, however, of the right order.

For the other pure solvents we have calculated the energy of activation necessary to account for the observed reaction velocities at 25°, assuming (I) that reaction occurs between peroxide molecules and iodide ions alone, and (2) that a solvent molecule participates in each effective collision. These values of E are given in the following table. The temperature coefficient of the viscosity of ethylene glycol was determined in an Ostwald viscometer with an accuracy sufficient for our purpose and the correction to be added to E was found to be 7350 Cal.

Solvent.				E (calc.). (1.)		E (calc.).	
Water Methyl alcohol Ethyl alcohol Glycol	:		•	13,760 16,810 17,790 14,300	17,730 18,690 18,160 17,560	13,640 16,520 15,530 12,550	

The results are of considerable interest in that they show that while in aqueous and methyl alcohol solutions, the solvent participates in the reaction; in the case of the ethyl alcohol solutions there is no necessity to introduce any hypothesis as to the action of the solvent, collisions between peroxide molecules and iodide ions alone being sufficient to account for the observed velocity. In the case of the glycol solutions it seems that a three-body collision again provides the mechanism for the reaction, but it must be admitted that the experimental difficulties preclude a decisive opinion on this point.

Finally for the water-methyl alcohol mixtures we have used viscosity data  $^{12}$  and calculated the values of E' given in the following table. As association probably occurs between methyl alcohol and water, we have used our data to calculate  $n_s$ , the number of solvent molecules participating in the effective collisions, and compared them with the total number  $(n_{\rm W}+n_{\rm A})$  of alcohol and water molecules present per c.c.

Alcohol.	E'.	$n_{\rm S} \times 10^{-22}$ .	$(n_{\mathbf{W}} + n_{\mathbf{A}}) \times 10^{-22}.$	
0·0	17,710	2·7	3·37	
25·5	19,670	0·3	3	
54·4	20,340	0·2	2·5	
87·8	19,870	0·3	2	
100	19,310	1·25	1·9	

#### Summary.

The temperature coefficient of the decomposition of hydrogen peroxide in the presence of potassium iodide has been studied. The reaction in aqueous solution proceeds in agreement with the rate calculated on the assumption that collisions between peroxide, iodide and water particles occur, the effective collisions being calculated from the temperature coefficient, after a correction based on the viscosity has been made. A similar hypothesis is successful in the case of methyl alcohol, while with

<sup>&</sup>lt;sup>12</sup> Bingham, White, Thomas and Caldwell, Z. physikal, Chem., 83, 641, 1913.

ethylene glycol as solvent agreement is obtained within the limits of experimental error. The hypothesis fails in its application to ethyl alcohol solutions, where, apparently, reaction occurs between peroxide and iodide directly.

Only very small variations have been observed in the temperature coefficient on addition of neutral salts to the aqueous solution.

The reaction in methyl alcohol-water mixtures can be explained satisfactorily on the hypothesis of three-body collisions, provided that reasonable assumptions are made regarding the degree of compound formation occurring in the solvent.

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# NOTES ON A PAPER BY MR. E. HATSCHEK ON "THE ELASTIC PROPERTIES OF GLYCERIN GELATIN GELS HARDENED WITH FORMALDEHYDE." 1

By H. J. Poole.

Received 24th October, 1933.

Mr. Hatschek's paper has been read with very great interest and appreciation. The way in which he has resisted "the strength of tradition or of habit" and has developed a technique diametrically opposed to that usually employed and which avoids many of the former difficulties is as clever as it is now obvious.

The existence of a thermal hysteresis as protracted as that shown is surprising. In the present writer's experiments <sup>2</sup> the ageing was always done at a lower temperature than that at which the measurements were made. The hysteresis was not so evident as it is in Mr. Hatschek's experiments where the specimens were kept at a steady temperature. In the case of gels of cellulose acetate <sup>3</sup> the course of the hysteresis was followed and the interesting observation made that the attainment of equilibrium was much more rapid from a lower temperature than from a higher one than that at which the measurements were made. It is possible that a similar phenomenon occurs with gelatin. An explanation is suggested in the paper (loc. cit.).

On page II29 a difficulty in connection with my explanation of the persistence of optical anisotropy is cited. If the phases are in dynamic equilibrium, however, there must be a continuous interchange of molecules between the rigid and the fluid phases just as much as in the case of a salt in contact with its saturated solution. It is not necessary to postulate fluctuations of temperature for this to occur, although in practice, of course, such variations always exist.

Mr. Hatschek's observation that the modulus decreases with compression is a most important addition to the evidence supporting the fibrillary theory of gels and its strength is increased by the further

observation that the modulus is increased in directions perpendicular to that of compression. This also follows from the theory. When a fibrillar structure is stretched the component fibrils all assume a trend towards the direction of stress. In very rough analogy the structure develops a fibrous character like timber and its strength along the grain becomes greater than across it.

The experiments on the orientation of gas bubbles generated in reversibly and irreversibly strained gels furnish further evidence in favour of the theory. For clearness the four cases are considered separately:

# (a) Reversible Elongation.

The axial stress is here greater than that perpendicular to the axis. The stress in the gel substance at the surface of the incipient bubble is due to the gas pressure in the bubble and to the externally applied stress. In the direction of the stress the internal pressure and the stress are cumulative but the applied stress has no component at right angles to its own direction. Hence rupture, which occurs, of course, at the most highly stressed zone, will set in along a diametral plane perpendicular to the line of stress. Further splitting in the same direction will then occur as the bubble grows in volume thus generating a lenticular bubble whose equatorial plane is perpendicular to the axis.

# (b) Reversible Compression.

This case is similar to the foregoing except that the sign of the stress is changed and instead of the plane perpendicular to the axis being the most highly stressed it is now the least and rupture will occur along planes at right angles to it. There are an infinite number of such planes parallel to the axis of compression and Mr. Hatschek's photographs clearly show the random distribution of the rupture planes parallel to the axis.

# (c) Irreversible Elongation.

The two cases just cited have not required the assistance of any theories of structure and similar phenomena would probably be obtained in any elastic medium colloidal or otherwise. The two cases of irreversible elongation are, however, different and depend upon the properties assumed by a fibrillar structure after permanent set has occurred. The evidence so far obtained suggests that in the state of permanent set all stress in the fibrils has disappeared but that they retain their strain. The tensile strength will be greatest in that direction in which the fibrils are most closely packed and in which as a consequence there are more per unit area of cross-section. This is, of course, the direction in which the gel has been stretched. If as in irreversible elongation the direction of stretching is along the axis the rupture will occur parallel to it and the bubbles will set themselves at random parallel to the axis.

# (d) Irreversible Compression.

In this case the direction of stretching is radial or perpendicular to the axis and the weakest direction is thus along the axis. Bubbles will therefore set themselves perpendicular to the axis.

These predictions agree exactly with Mr. Hatschek's experimental findings. The behaviour is paradoxical at first sight, but it seems to have furnished a valuable piece of evidence in favour of the fibrillary theory. It may even be possible to use the method for discriminating between gels possessing a fibrillary structure and any which may not.

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# CAPILLARY ASCENT OR DEPRESSION OF LIQUIDS IN CYLINDRICAL TUBES. PART II. WIDE TUBES.

By Alfred W. Porter, F.R.S.

Received 25th October, 1933.

In a previous paper in these Transactions I have worked out the capillary ascent (or depression) for tubes of radii up to values of  $r/\beta$  equal to 3 and the reduced meniscus heights,  $h/\beta$ , which correspond, making use of Bashforth and Adams Tables. Rayleigh 2 had worked out a formula giving the shape of the meniscus for wide tubes and had calculated  $h/\beta$  and  $h_0/\beta$  for values of  $r/\beta$  from 6 to 10 and a contact-angle of 0°.

It is possible to extend these calculations of Rayleigh by following his method and so obtain values for various angles of contact as well as (if necessary) for still wider tubes up to  $r=\infty$ . The formula, in fact, becomes more exact the *wider* the tube considered.

It is important to notice that, if the shape of the meniscus has been determined for the contact-angle of  $0^{\circ}$  and a given radius, the same shape will hold good for a larger angle and a corresponding less radius. Hence if a plot is made of the menisci for various values of  $r/\beta$  and the whole diagram be traversed by lines of constant contact angle, the points of intersection of the two sets determine the values of r and h which correspond.

Such a diagram was shown in the former paper in Fig. 1. This shows the general trend but is too small for actual use. The diagram actually made use of was on a much larger scale. This diagram has now been extended to include the Rayleigh values. Moreover constantangle lines for every 10° have now been drawn upon it. Rayleigh's formulæ do not hold for values of  $r/\beta$  much less than 6; it follows that there still remains a gap between these and the values recorded in my former paper; i.e., for  $r/\beta$  from 3 to 6.

It is interesting to notice that this gap is a region in which maximum values of  $h/\beta$  occur. I have previously indicated that the Bashforth and Adams Tables give increasing values of  $h/\beta$  for increasing  $r/\beta$  whereas Rayleigh's formulæ for wide tubes give decreasing values. For 90° inclination the ordinate changes very slowly from 1.57 at the maximum to 1.414 at  $r/\beta = \infty$  whereas the value obtained from Bashforth and

TABLE OF CAPILLARY CORRECTIONS FOR WIDE TUBES.

1.5.		0.0050	9680.	.0148	.0059	1 .00222	06000.	1
r.4.		8860.0	.0395	.0146	6500.	.00221	06000-	.00034
1.3.		0.0915	.0384	.0142	.0058	91700.	680000	-00034
1.2.		0.0885	1260.	.0138	.0057	.00211	L8000.	9000
I'I.		0.0844	.0326	.0132	.0055	.00203	-00084	.00034
1.0		9620.0	.0335	.0126	.0052	£6100.	82000.	66000.
0.6.0	β.	0.0740	.0312	2110.	.0049	.00180	.00074	10000.
0.8	Values of $h_0/\beta$ .	0890.0	0.0289	.0108	5†00.	.00163	69000.	00000
0.7.	Vah	o.ogio	.0258	2600.	.0040	.00146	.00003	.00027
9.0	Andreas de Contra de Contr	0.0530	÷250.	.0085	9£00.	.00128	.00056	.0003
0.2.		0.0449	.0185	2200.	.0030	01100.	.00047	01000.
0.4.		0980.0	8410.	.0058	-0024	.00088	.00039	91000.
0.3.		0.0272	.0113	.0044	8100.	99000.	06000.	11000.
0.3.		0.0180	2200.	.0029	.0012	-00044	.00020	80000.
в. от.		06000.0	9600.	.0015	9000.	.00022	01000.	¥0000.
IIIB.	ν/β.	4	5.	9	7	×	0	IO

Adams is about 1.44 at  $r/\beta=3$ . It is possible therefore with considerable reliability to fill up the gap with curves of slight curvature and to make use of them in determining the corresponding capillary ascents. I have done this for every 10° contact angle.

The values obtained for this intercalated region are shown in the table in italics as an indication that they are not so reliable as the rest. Hence the problem is approximately solved up to  $r/\beta = 10$  and it can easily be extended to tubes of any greater width if necessary.

Rayleigh's formula 3 for the shape is

$$\begin{split} \frac{R-r}{\beta} &= \log \left\{ \sqrt{2} - 1 \right\} + \sqrt{2} + \frac{\beta}{3R} \left\{ -2 + \frac{\sqrt{2}}{2} + \frac{3}{2} \log \left( \sqrt{2} - 1 \right) \right\} \\ &- \log \tan \theta / 4 - 2 \cos \theta / 2 \\ &+ \frac{\beta}{3R} \left\{ \frac{1}{2(1 + \cos \theta / 2)} + 2 \sin^2 \theta / 2 - \frac{3}{2} \log \left( \tan \theta / 4 \right) \right\}. \end{split}$$

where I have put R as the abscissa when the contact angle is  $0^{\circ}$  (or  $\theta = 90^{\circ}$ ) and r is the abscissa when the inclination of the curve is  $\theta$  (i.e., contact angle is  $90^{\circ} - \theta$ ). The corresponding formula for  $h_0/\beta$  is

$$R/\beta - \log \beta/h_0 = 0.8381 + 0.2798 \beta/R + \frac{1}{2} \log R/\beta.$$

The values of  $h_0/\beta$  for various values of  $h/\beta$  and  $r/\beta$  are recorded in the accompanying table which forms an extension of the table previously given (loc. cit.1)

#### Addendum.

The following data, A and B, which are calculated by aid of Rayleigh's formulæ enable the full diagram of contours to be constructed. This diagram is the basis of the data given in this paper.

A.

8.	90°.	8o°.	70°.	60°.	50°.	40°.	30°,	20°.	ro*.
R/β.				V	alues of	$h/\beta$ .			
6 7 8 9	1·571 1·549 1·532 1·519 1·508	1·381 1·367 1·357 1·349 1·343	1·2345 1·2221 1·2127 1·2054 1·1996	1.0780 1.0669 1.0585 1.0520 1.0468	0·9125 ·9029 ·8957 ·8901 ·8856	0·7397 ·7317 ·7258 ·7211 ·7174	0·5601 ·5540 ·5495 ·5459 ·5431	0·3730 ·3718 ·3687 ·3663 ·3644	0·1897 ·1875 ·1859 ·1846 ·1836

B.

	θ.	90°.	80°.	70°.	60°.	50°.	40°.	30°.	20°.	10°.
$R/\beta$ .	$h_0/\beta$ .				Val	ues of	r/β.			
6 7 8 9	·0149 ·0059 ·0023 ·00089 ·00034	6 7 8 . 9	5·988 6·988 7·988 8·988 9·988	5·949 6·949 7·949 8·949 9·950	5·875 6·876 7·877 8·877 9·878	5.759 6.761 7.762 8.763 9.764	5·584 6·588 7·591 8·593 9·595	5·327 6·333 7·338 8·342 9·345	4·926 5·936 6·944 7·950 8·956	4·199 5·217 6·231 7·242 8·251

<sup>3</sup> Formula 52, loc. cit.

<sup>&</sup>lt;sup>4</sup> Formula 60, loc. cit.

## SOME PHYSICAL PROPERTIES OF MIXTURES OF CERTAIN ORGANIC LIQUIDS.

By Violet Corona Gwynne Trew and Gertrude Margaret Clare Watkins.

Received 12th October, 1933.

A number of physical properties of mixtures of certain alipahtic saturated alcohols have been investigated in order to compare the value of the various properties in studying deviations from the Mixture Rule and hence the conditions existing in liquid mixtures. The value of determinations of magnetic susceptibility in giving indications of such deviations was especially considered.

Four sets of mixtures were investigated each containing normal butyl alcohol as one constituent with normal propyl, isobutyl, isopropyl or  $\gamma$ -amyl alcohols as the other constituent. These liquids are members of a closely related aliphatic series so would be expected to show only small deviations. For purposes of comparison, a fifth mixture was considered, in which the two constituents were widely dissimilar and so would probably show marked deviations on mixing. Acetone and trichlor-ethylene, which contains both an unsaturated linkage and the strongly electro-negative chlorine atoms, were chosen as the pair of liquids for this mixture. Hence it was hoped that a good indication would be obtained of the relative suitabilities of magnetic susceptibility and other properties for investigating deviations in liquid mixtures, both in the case of related and widely differing substances. The properties measured include density, refractive index, magnetic susceptibility, and for some sets of mixtures viscosity, specific heat and heat of mixing.

#### Experimental.

A number of mixtures, in some cases seven and in other cases nine, of the two constituent liquids was made up accurately as described in a previous communication, after rigorous purification of the constituents. Table I. gives the physical constants as determined for each of the pure liquids. Measurements of density, refractive index, viscosity, specific heat and heat of mixing were made as described previously. Density determinations were made to the fifth place for mixtures showing slight deviations, to the fourth place for the acetonetrichlorethylene mixture which gave more marked deviations. Measurements of magnetic susceptibility were carried out by means of a modified Gouy method using an apparatus similar in principle to that described recently by Sugden.2 A column of the liquid under investigation, of constant length, was suspended vertically so that the lower end was in a maximum homogeneous magnetic field, and the upper end in a region of no field. The force F exerted as a vertical pull on a material of permeability  $\mu_1$  suspended in a medium of permeability  $\mu_2$  is given by

$$F = \frac{\mu_1 \, - \, \mu_2}{8 \, \pi} \, . \, A (H_1{}^2 \, - \, H_2{}^2)$$

<sup>&</sup>lt;sup>1</sup> Trew, Trans. Faraday Soc., 28, 509, 1932.

I.	II.	III.	IV.	v.	VI.	VII.	VIII.	IX.
Liquid.	B.Pt.	Mean Density.	Refractive Index.	Viscosity.	Specific Heat.	Mass Suscept.	Molecular Suscept.	Molecular Suscept.
	Degrees Centigrade.	D <sub>25</sub> .	n <sup>25</sup> .	η25.	Calories per Gram.	- 106 χ <sub>m</sub> .	(Calc.)	From Pascal's Values.
N-butyl alcohol . N-propyl alcohol . Iso-propyl alcohol . Iso-butyl alcohol . Iso-y- methyl- butyl (y amyl	117·25 <sub>780</sub> 96·6 <sub>774</sub> 81·6 <sub>745</sub>	o·8o849 o·8o236 o·78343 o·8o041	1·39748 1·38343 1·37538 1·39387	0·025641 0·019666 0·020087 0·033556	0·591 — 0·650 —	0·7908 0·7870 0·7930 0·8094	58·58 47·22 47·63 59·89	58·3 46·4 46·4 58·3
alcohol). Acetone. Trichlor- ethylene	130·1 <sub>749</sub> 55·80 <sub>760</sub> 86·60 <sub>758</sub>	0.81286 0.7847 1.4550	1·40781 1·35730 1·47488	°°°37563 — —	0·513 0·227	0.8060 0.5772 0.4961	70·93 33·5 <sup>2</sup> 65·15	70·2 33·9 67·9

TABLE I.—Physical Constants of Pure Liquids Used.

where  $H_1$  is the field at the lower,  $H_2$  at the upper end and A is the area of cross-section of the material. If  $H_2$  is zero and  $\mu=4\pi\chi$ . d where  $\chi$  is the magnetic mass-suceptibility and d the density then

$$\chi = \frac{2El}{w(H_1^2)} + \frac{(\chi \cdot d)_{air} \cdot lA}{w}$$

(where l= length of column, w the weight of liquid in the column, and substituting for d=w/lA). Of these quantities  $(\chi\cdot d)_{air}$  is  $=0.03\times 10^{-6}$  v and w are directly measured,  $H_1$  is constant for a given aperture of pole piece, l is constant for a given length of material whence

$$10^6 \chi = \frac{\alpha F}{w} - \frac{V \cdot 0.03}{w}$$

where  $\alpha$  is a constant for the apparatus using a constant length of material. If F is measured in milligrams, w in grams, v in cubic centimetres then

$$\alpha = \frac{2l \times 10^6 \times 981}{H_1^2 \times 1000}.$$

For the present investigation with liquids, a balance of the Bunge type was used, sensitive to 0.01 of a milligram, modified so that the lever was worked from the right-hand side. The left-hand scale pan and support were replaced by a light aluminium support and a disc of the same dimensions as the right-hand pan, which carried on its lower side a hook. From the hook was suspended a fine platinum wire which passed through a hole in the floor of the balance-case and bench. To the lower end of this wire was attached a copper stirrup from which was suspended the tube containing the liquid under investigation. The length of platinum wire was adjusted so that the inside meniscus of the bottom of the tube was exactly level with a mark on the centre of the pole pieces of an electromagnet arranged so that the gap between the pole pieces came vertically beneath the hole in the bench. The pole pieces of the electro-magnet

were detachable so that a variety of pole pieces could be used with the same

magnet.

Since switching on the electro-magnet caused a considerable movement of the pole pieces towards each other, these were maintained at a constant distance by a brass distance piece kept in position on the top of the pole pieces by means of screws, and with a circular hole in the centre through which the tube containing the liquid passed freely. By having a number of distance pieces of varying sizes the distance between the pole pieces and hence strength of the field could be varied over a wide range.

Experiments were carried out to determine the best aperture and strength of field to use, and it was found that a current of 3 amperes and 220 volts passing through magnet coils of 20,000 turns produced a field of about 5000 gauss, when the aperture between the pole pieces was 1.2 cm. This aperture and field gave the largest pull for the liquids investigated. The aperture was maintained at 1.2 cm. throughout the experiments with organic liquids, although for other substances other apertures might be more convenient.

The amperage was controlled by means of a variable rheostat, in series, and was registered by an ammeter in the circuit. A two-pole switch was employed to switch the current, supplied by the mains, on and off.

The field vertically above the pole pieces was then explored, in a number of experiments in which the tube was filled with water and gradually raised using a shorter and shorter suspension. At a height of 5 cm. above the centre of the pole pieces, the pull was only I per cent. of its original value becoming zero at 6 cm. above the mark. Hence in all determinations a column of liquid between 6.5 and 7.5 cm. in length was used, a mark being etched on the tube and the volume determined to this point. In this way a constant length l and volume V were ensured and the upper level of the liquid under investigation was well within the region of zero field. The field was constant for o.4 cm. either side of the centre mark ensuring that, even when weighing by oscillations, the bottom of the liquid was always well within the region of uniform maximum field.

The pull on a known volume of liquid was determined in the following The tube was weighed with the magnetic field off and then on, the liquid was measured out by means of a pipette constructed to deliver the volume of liquid to fill the tube exactly to the mark. The tube and liquid were then weighed in and out of the field. The value for the pull on the empty tube was redetermined during the course of the experiments and was found to be sensibly constant, hence an average value was taken and used throughout, being subtracted in each case from the total pull

on the liquid and tube.

Weighings were made to o or mg. the last place being determined by the oscillation method, using standardised weights and allowing only small amplitudes of swing to ensure that the tube did not swing out of the uniform field. The magnet and all apparatus below the bench was boarded in to prevent draughts. In addition, the suspension from the bench down to the top of the stirrup was surrounded by a copper tube to shield from draughts and sudden changes of temperature. The readings in and out of the magnetic field were made very rapidly so that they should be made at the same temperature as nearly as possible. A thermometer was placed between the pole pieces, and results were considered untrustworthy if the temperature rose more than 1° C. during the determination, as convection currents might be set up which would affect the readings. In order to avoid heating effects the current was kept on for as short a time as possible. The magnet coils were cooled between readings Even with these precautions variations of 0.05 mgrms. by an electric fan. were sometimes found, which were between 0.5-1.5 per cent. of the total pull. To minimise these, each reading was repeated several times and an average value taken.

TABLE II.

Mixture.	Gram Mol. Per Cent. n-Butyl Alcohol.	Density D <sup>25</sup> <sub>25</sub> .	Refractive Index at 25°.	Viscosity at 25°. #10.3	Mass Susceptibility at 25°. $x - 10^6$ .
N-Butyl Al	cohol—Iso-Pr	opyl Alcoho	ol.		
Iso-propyl	1				
alcohol	0	0.78343	1.37538	2.0087	0.7939
I.	10.26	0.78662	1.37810	2.0571	0.7936
ıî.	20.12		1.38086	2.1048	0.7952
111.	30.20	0.78946	1.38325	2.1452	0.7947
IV.		0.79242	1.38560	2.2074	0.7963
V.	40.45	0.79533		2.2686	0.7974
VI.	50.86	0.79776	1.38767	i .	0.7962
	60.02	0.79991	1.38967	2.3274	
VII.	73.40	0.80318	1.39233	2.4017	0.7975
VIII.	79-64	0.80462	1.39386	2.4371	0.7969
IX.	90.21	0.80675	1.39580	2.5059	0.7944
n-butyl alcohol	100	o·8o888	1.39747	2.5628	0.7916
		mari Alcohol		-	
A-Dutyl A	lcohol—n-Pro	pyi Aiconoi	•		
N-propyl	1	_	1		
alcohol	0	0.80236	1.38343	1.9666	.7870
I.	10.09	o·80331	1.38513	2.0241	.7874
II.	20.00	0.80402	1.38674	2.0816	.7878
III.	30.13	0.80460	1.38820	2.1355	.7899
IV.	40.26	0.80544	1.38987	2.1945	.7905
V.	50.09	0.80605	1.39128	2.2540	.7926
VI.	60.55	0.80653	1.39259	2.3189	.7941
VII.	62.79	0.80663	1.39293	2.3261	·794I
VIII.	79.83	0.80735	1.39504	2.4316	.7940
IX.	89.92	0.80792	1.39634	2.4941	.7933
n-butyl	09 92	0 00/32	- 33-31	1	,
alcohol	100	0.80841	1.39749	2.5750	.7916
N-Butyl A	lcohol—Iso-B	utyl Alcoho	1.		
Iso-butyl			1	1	1
alcohol.	0	0.80041	1.39387	3.5556	0.8094
I.	9.82	0.80117	1.39426	3.2385	0.8102
ıi.	20.07	0.80219	1.39474	3 1106	0.8111
III.	30.10	0.80292	1.39518	3.0157	0.8112
IV.	40.46	0.80378	1.39548	2.9354	0.8101
v.	50.26	0.80441	1.39584	2.8590	0.8080
VI.	62.61	0.80536	1.39638	2.7724	0.8069
		0.80613	1.39658	2.7262	0.8025
VII.	70.24	0.80671	1.39690	2.6719	0.7995
VIII.	80.01	0.80780	1.39719	2.6076	0.7925
IX.	91.78	0.80700	1 39/19	20070	13.3
n-butyl alcohol	100	0.80839	1.39749	2.5569	0.7900
N-Butyl A	lcohol—Iso-γ	-Methyl=Bu	tyl=Alcohol (	γ-Amyl).	
γ-amyl	1				. 0-6
alcohol	0	0.81286	1.40781	3.7563	0.8060
I.	10.33	0.81241	1.40706	3.6200	0.8056
II.	20.40	0.81191	1.40625	3.4722	0.8057
III.	29.77	0.81153	1.40538	3.3435	0.8031
IV.	40.26	0.81112	1.40449	3.2102	0.8001
V.	50.05	0.81067	1.40350	3.0928	0.7974
VI.	60.46	0.81033	1.40216	2.9719	0.7965
VII.	69.96	0.80988	1.40128	2.8507	0.7945
VIII.	80.15	0.80923	1.40010	2.7457	0.7868
IX.	91.72	0.80871	1.39871	2.6152	0.7833
n-butyl	- 1	1			
alcohol	100	0.80827	1.39749	2.5617	0.7776
		1	1	*	

The magnetic susceptibility was then calculated from the formula, the value of  $\alpha$  having previously been obtained by a series of experiments with pure crystalline solids, and certain pure organic liquids, of well established susceptibility. Crystalline copper sulphate, nickel ammonium sulphate, ferrous sulphate and ferrous ammonium sulphate were used for the solids and acetone, benzene and chloroform for the liquids. The values obtained for  $\alpha$  using the solids differed by as much as 5 per cent., while those obtained for the liquids differed among themselves by only 0.5 per cent. The mean of both sets of readings was, however, the same, i.e.,  $\alpha = 0.660$ . This value was therefore used throughout the subsequent experiments.

#### Results.

Table I. shows in columns II.-VII. the physical constants determined for each of the pure liquids, while column VIII. gives the molecular susceptibilities which are in good agreement with the theoretical values in column IX. calculated from Pascal's atomic susceptibility data. Tables II. and III. give the experimental values of the various physical properties measured for each of the mixtures, and Tables IV. and V. show the calculated percentage deviations of these from the theoretical figure required by the mixture law.

Mixture.	Gram. Mol. Per Cent. Trichlor.	Density $D^{25}_4$ .	Mass Suscept. $x - 10^6$ .	Gram. Mol. Per Cent. Trichlor.	Refract. Index.	Gram. Mol. Per Cent. Trichlor.	Specific Heat in Calories per Gram.	Heat of Mixing in Calories per Gram.
Acetone I. II. III. IV. V. VI. VIII. VIII. Trichlor- ethylene	0 11·55 27·04 39·04 48·07 59·32 75·53 88·74	0·7847 0·8782 0·9963 1·081 1·143 1·217 1·316 1·392	0·577 0·564 0·542 0·530 0·523 0·520 0·513 0·503	0 12·32 30·32 49·94 63·93 71·76 79·78 89·38	1·35730 1·37489 1·39876 1·42393 1·43823 1·44605 1·45488 1·46453	0 12·10 29·64 46·76 63·93 72·36 79·78 89·38 89·86	0·513 0·453 0·390 0·337 0·297 0·283 0·285 0·257	0-43 1-05 1-20 0-86

TABLE III.—ACETONE-TRICHLORETHYLENE.

#### Discussion of Results.

N-Butyl-Iso-Propyl Alcohols.—If the percentage deviation is plotted against composition it is found that all properties show marked deviations from the mixture rule. Density, refractive index and viscosity give curves with a slight but clearly marked displacement of the point of maximum deviation toward the iso-propyl alcohol end. The magnetic-susceptibility curve, however, shows a shift of maximum towards the n-butyl alcohol end.

These deviations may probably be explained as due to a certain degree of co-ordination between the molecules of the two alcohols concerned, and secondly to alterations in the degree of association of each pure constituent by addition of molecules of the other. The density, viscosity and refractive index deviations would indicate deassociation of the *iso*-propyl alcohol in presence of the normal butyl alcohol. The

TABLE IV .- Percentage Deviations.

No of Mixture.	Density.	Refract. Index.	Viscosity.	Mass Suscept.	Density.	Refract. Index.	Visc.	Mass Suscept.	
		utyl—iso- it. gm. m calcu				nbutyl—γ-amyl alcohols. Per cent. gm. mol. deviation from calculated.			
Ι.	0.073	0.033	0.41	0.00	0.002	0.029	0.36	0.30	
11.	0.112	0.075	0.74	0.23	0.001	0.039	1.12	0.67	
III.	0.165	0.087	1.41	0.10	0.005	0.046	1.68	0.70	
IV.	0.203	0.093	1.14	0.43	0.013	0.023	1.98	0.97	
V.	0.174	0.077	0.95	0.59	0.013	0.061	2.06	0.71	
VI.	0.120	0.073	0.59	0.47	0.031	0.044	2.04	0.97	
VII.	0.133	0.053	0.56	0.68	0.028	0.048	2.39	1.06	
VIII.	0.114	0.060	0.53	0.62	0.006	0.040	1.93	0.44	
IX.	0.046	0.036	0.10	0.34	0.007	0.026	1.69	0.43	
		l alcohol— t. gm. mo calcu			nbutyl—iso-butyl alcohols.  Per cent. gm. mol. deviation from calculated.				
I.	0.042	0.020	0.10	0.00	0.000 1	0.003	1.18	0.33	
II.	0.056	0.036	0.32	0.00	0.002	0.010	2.67	0.69	
III.	0.052	0.041	0.65	0.23	0.001	0.016	3.16	0.94	
IV.	0.079	0.055	0.72	0.27	0.001	0.011	3.20	1.06	
V.	0.076	0.057	0.76	0.48		0.011	3.22	1.04	
VI.	0.063	0.046	0.70	0.61	0.001	0.017	2.91	1.10	
VII.	o∙o58̃	0.048	0.90	0.60	0.001	0.012	2.44	0.91	
VIII.	0.020	0.029	0.82	0.21	0.001	0.016	1.64	0.70	
IX.	0.015	0.019	0.78	0.39	0.001	0.000	0.56	0.01	
						1			

TABLE V.—Acetone—Trichlorethylene. Percentage Deviation from Calculated.

No. of Mixture.	Density.	Mass Susceptibility.	Refractive Index.	Specific Heat.
Acetone . I.	o 1.88	o 0·704	o o·226	o 5.23
II.	3.18	2.34	0.412	8.88
III. IV.	3·35 3·35	2·75 2·79	0·559 0·402	10.00
v.	3·05	1.70	0.303	7.52
VI.	2.02	0.570	0.260	5.61
Trichlor-	0.48	0.370	0.152	3.21
ethylene .	0	0	0	0

magnetic susceptibility curve would indicate deassociation of the normal butyl alcohol. The fact that all properties do not show a shift in maximum to the same side would suggest that at least two effects are taking place, some properties showing the one more markedly than others.

N-Butyl and N-Propyl Alcohols.—In the case of all the properties investigated, deviations on mixing these two alcohols were less than those using *iso*-propyl alcohol. Deviations were, however, obtained, showing some degree of co-ordination between these two alcohols, but probably less than for the previous two. As before, the curves are

not entirely symmetrical about the 50 moles. axis, density and refractive index curves showing a slight shift to the *n*-butyl alcohol end. This would again indicate that changes in the degree of association of each pure constituent are brought about on addition of the other.

N- and Iso-Butyl Alcohols.—In the case of these two alcohols density and refractive index curves show very small deviations, but viscosity and mass susceptibility show even larger deviations than in the case of either of the two former mixtures. The magnetic susceptibility curve is very nearly symmetrical. The viscosity curve shows a definite shift in the direction of mixtures containing a higher proportion of iso-butyl alcohol, while the maximum of the refractive index curve is indefinite.

These results are difficult to correlate as the viscosity and magnetic susceptibility deviations would indicate a considerable amount of coordination, the density and refractive index curves indicating little or no co-ordination. This may be due to some fundamental difference in the extent to which the various deviations may be considered as due to the same causes. The evidence further indicates for this mixture that only slight changes in the degree of association of the original

pure liquids result on mixing them.

N-Butyl and Iso- $\gamma$ -Methyl-Butyl Alcohols ( $\gamma$ -Amyl Alcohol).—For this mixture all properties show deviation, the density and refractive index deviations being small as in the previous case. The viscosity deviations are large, being slightly less in magnitude than those of the last mixture. The mass susceptibility deviations are also of about the same magnitude as those for the two butyl alcohols. The susceptibility and density curves are almost symmetrical, mixtures having a higher proportion of the n-butyl alcohol showing if anything a slightly greater deviation. This tendency is considerably more marked with the viscosity curve which would indicate deassociation of the n-butyl alcohol on addition of the iso-amyl alcohol. The refractive index deviation curve, like that of the susceptibility is practically symmetrical. Here again, then, we find different maxima given by the different property-deviation curves.

Acetone-Trichlorethylene.-As would be expected, in the case of this mixture considerably greater deviations were obtained for all properties, even refractive index deviations being about five times greater. All properties investigated showed considerable deviations. There was a marked evolution of heat on mixing the two liquids as shown by the heat of mixing curve, whereas in the case of the mixtures of alcohols, determination of heat of mixing had to be abandoned owing to the very slight changes obtained. The most marked deviations of all properties investigated occurred with the specific heat. Mass susceptibility deviations were quite considerably larger than in the case of mixtures of the alcohols. On plotting the percentage deviations against composition all properties showed a displacement of the maximum to the acetone end. The position of the maximum was the same for all properties, being between 40-50 moles per cent. of trichlorethylene. These results would clearly indicate definite co-ordination between these two liquids on mixing, and secondly, deassociation of the associated acetone molecules on addition of trichlorethylene. Such results are in agreement with these previously found for mixtures of acetone and bromoform.1

#### General Conclusions.

The alcohols investigated may be represented by the general formula  $R_n$ —0—H and belong to the class of hydroxy-compounds in which the oxygen atom is capable of donating two electrons to an adjacent

hydrogen atom to give a co-ordination compound, i.e.,  $H-O \rightarrow H-O$  Obviously the orginal pure alcohols will tend to be highly associated in this way, and a number of possibilities for co-ordination complexes arises on mixing two of the alcohols. The changes taking place are therefore somewhat complicated as is indicated by the experimental results given above. In the case of the mixture of acetone and trichlorethylene it would appear from the similarity of results given by the various physical properties that the changes are less complex, probably deassociation of the constituents and a definite co-ordination compound between the acetone and the trichlorethylene. The position of the maximum would indicate this as either due to one molecule of acetone co-ordinated with one of trichlorethylene and a shift due to deassociation of the acetone or to two molecules of acetone co-ordinated with one of trichlorethylene.

If the latter is the case, i.e.,

$$\label{eq:ch3} \mbox{2CH}_3 \,.\, \mbox{CO} \,.\, \mbox{CH}_3 + \mbox{C} \,.\, \mbox{H} \,.\, \mbox{Cl} \,:\, \mbox{CCl}_2 \rightleftharpoons \mbox{C(CH}_3)_2 (\mbox{OH}) -- \mbox{C(H)} (\mbox{Cl}) -- \mbox{C(Cl}_2) \\ \mbox{C(CH}_3)_2 (\mbox{OH})$$

the maximum should be at 33 moles. per cent. trichlorethylene and the observed maximum at 40-45 moles. of trichlorethylene would indicate a shift due to deassociation of trichlorethylene. Deassociation of acetone may also have occurred but to a less extent than for the trichlorethylene. This latter would appear to be the most probable explanation.

A general consideration of the various properties investigated shows that density and refractive index give similar results and minimum deviations, and might be expected to be least suitable for investigating deviations from the mixture law. This, however, is somewhat offset by the ease with which accurate results to at least five decimal places can be obtained in both cases with simple apparatus. The variation in maxima shown by the different properties for the same mixture would appear to indicate that the properties do not necessarily depend on changes taking place in the mixtures in the same way. The results do not give any indication of a rule that may be applied to elucidate this.

Magnetic susceptibility and viscosity give similar high deviations, but in the case of viscosity measurements considerable care is required to ensure accurate results. In the case of magnetic susceptibility measurements, as described, the results can probably be considered as accurate to 0.5 per cent. As the maximum deviation for the mixtures of alcohols considered was only I per cent. it is perhaps not surprising that the curves show dissimilarities. That some of this may be due to experimental error is possible and would be supported by the agreement found in the case of mixtures having higher deviations. In general, however, the magnetic susceptibility gives clear indication of deviations from the mixture law and hence is a suitable property to consider with others in investigating such deviations.

#### Summary.

1. Every mixture investigated showed some departure from the additive mixture law, so that none of these pairs of liquids can be regarded as ideal.

2. The deviations obtained indicate co-ordination between the two constituents, together with deassociation of previously associated molecules

of the pure constituent.

3. All properties investigated are not necessarily equally modified by changes occurring on mixing the two liquids as is indicated by the variation in the position of the maximum.

4. Density and Refractive Index give similar low deviations but are

not very susceptible to unavoidable experimental error.

5. Viscosity and Mass Susceptibility give similar high deviations, but in the methods used the experimental error is higher than for the other two properties. Magnetic mass-susceptibility measurements are equally suitable for considering with other properties in measuring deviations from the mixture law.

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## THE DISSOLUTION OF MAGNESIUM IN AQUEOUS SALT SOLUTIONS. PART III.

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The broad principles of the electrochemical theory of corrosion are now generally accepted, but the actual mechanisms of the anodic and cathodic reactions are not satisfactorily known. In the case of a metal dissolving in sodium chloride solution the view commonly held is that the anodic product is the metal chloride and the active cathodic product alkali, left by discharge of hydrogen ions. If the metal chloride is soluble, interdiffusion of the electrode reaction products results in the formation of metal hydroxide, which, if sparingly soluble, may assume one or more of a variety of forms and may even, by some obscure mechanism, adhere tightly to the metal surface and prevent further attack.

In Part II., it was stated that the initial rate of attack of magnesium was the same in 0·1N and 0·002N sodium chloride solutions and in 0·1N sodium sulphate solution, a fact which does not accord with the view expressed above, unless cathodic control is assumed. The cathodic reaction for magnesium takes place with such ease that hydrogen depolarisation by dissolved oxygen has never been detected, the discharged hydrogen being equivalent always to the metal dissolved, a fact which renders cathodic control unlikely.

<sup>&</sup>lt;sup>1</sup> Trans. Faraday Soc., 29, 853, 1933.

Experiments described in this part enable the view, already expressed briefly in Part II., of primary preferential hydroxyl ion discharge at the anodes, to be confirmed. It will be shown also that the theory of primary hydroxyl ion discharge is supported by theoretical considerations.

Metal used corresponded to MgC2 and MgC3, the analyses of which have been given in Part I.<sup>2</sup> and experiments were performed in quad-

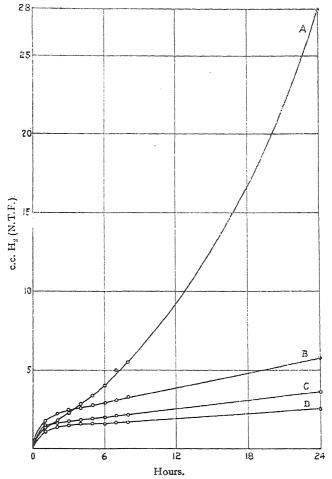


Fig. r.—Dissolution/time curves in various salt solutions. A = N, KCl. B = N. K<sub>2</sub>SO<sub>4</sub>, C = N. KBr. D = N. KI.

ruplicate, two experiments from each of the two samples of magnesium; mean curves are shown from these four experiments. Specimens used were  $I \times 4$  cms. with a punched hole 4.5 mms. diameter for suspension; other experimental details were the same as those described in Part I.

Figs. I and Ia respectively show later and initial dissolution/time curves in IN solutions of potassium chloride, bromide, iodide and

<sup>&</sup>lt;sup>2</sup> Trans. Faraday Soc., 29, 415, 1933.

sulphate. Large differences in the rates of reaction were observed in the later stages of the attack, but during the first few minutes the rates were almost identical.

Fig. 2 shows later and initial dissolution/time curves in the above solutions diluted to 0.001N. The rates of reaction were practically the same throughout and unlike those in the concentrated solutions showed only small differences after 24 hours.

Fig. 3 shows the later and initial dissolution/time curves in distilled water, in saturated magnesium hydroxide solution and in 0.001N potassium hydroxide solution. The initial rates of attack were again almost identical for each solution, and a comparison of Figs. 1a, 2 and 3 shows

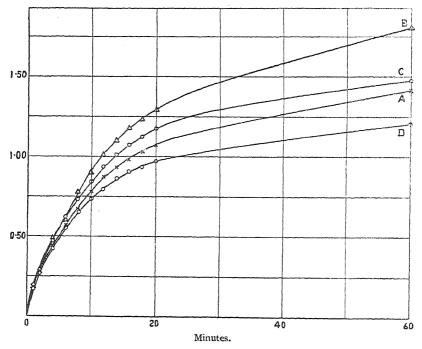


Fig. 1a.—Dissolution/time curves in various salt solutions. Initial action. A = N. KCl. B = N.  $K_2SO_4$ . C = N. KBr. D = N. KI.

that the initial reaction rates were of the same order, irrespective not only of the nature of the solution, but of its dilution.

Table I. shows clearly this important point, and also shows that the identity of the reaction rates ceases with time; the reading immediately before the 2-hour point was I hour, and that immediately before the 6-minute point was 4 minutes.

There was a definite tendency for the dilute solutions to show a slightly higher initial rate of reaction than the concentrated solutions, a fact which would not be predicted by the usual version of the electrochemical theory of corrosion but which is to be expected on the theory of primary hydroxyl ion discharge.

The Case for Anodic Control.—The suggestion of preferential hydroxyl ion discharge to explain the identity of the initial rates of

TABLE I.—Rates of Dissolution of Magnesium in Various Solutions after 6 Minutes and After 2 Hours.

	N KCI.	N KBr.	N KI.	N K <sub>2</sub> SO <sub>4</sub> .	o'ooi N KCL	o'ooi N KBr.	0.001 N KI.	o'oot N K <sub>2</sub> SO <sub>4</sub> .	o'oor N KOH.	Satd. Mg(OH) <sub>s</sub> Solution.	Water.
C.c.s $H_2/2$ mins. after 6 minutes.  C.c.s $H_2/$ hour after	0.13	0.15	0.13	0.13	0.15	0.17	0.18	0.17	o•16	o·16	0.12
2 hours .	0.40	0.18	0.19	0.37	0.05	0.08	0.10	0.05	0.05	0.08	0.10
2-00											
i	1		1				-		-		
	-			-							
# 8 B	15.3	-0-0	-0-0	AND THE PROPERTY OF THE PROPER							
1-50	A S	00									
			-0-								
			- ~ ~					0	и 100-и	KI	

Fig. 2.—Dissolution/time curves in dilute salt solutions.

Broken curves are later stages.

Hours. Minutes.

8

20

-0-0.001 N. KCL

16

40

attack tacitly assumes anodic control, an assumption which is, however, supported by facts. Hydrogen is so easily discharged at the cathodes that oxygen is never absorbed; dilution of the solution actually slightly increases the initial rate of attack, and the enormous lowering of the hydrogen ion concentration represented by 0.001N potassium hydroxide solution ( $p_{\rm H} \ll 12$ ) does not lower the initial rate of attack. The argument may be advanced that the alkaline solution should cause an increase

in the initial rate of reaction, owing to increase in the hydroxyl ion concentration. It is shown later, however, that the solubility of magnesium hydroxide is depressed in 0.001N potassium hydroxide, hence causing a greater rate of magnesium hydroxide film formation with a consequent greater rate of autoprotection.

A reaction under cathodic control should, moreover, be increased in rate by addition of substances capable of facilitating hydrogen evolution. such as saponin which increases the rate of dissolution of magnesium in certain artificial sea-waters.3

Traces of saponin were added to water and to 0.001N potassium hydroxide solution and the rates of dissolution of magnesium therein compared with those in the same solutions without saponin. A slight

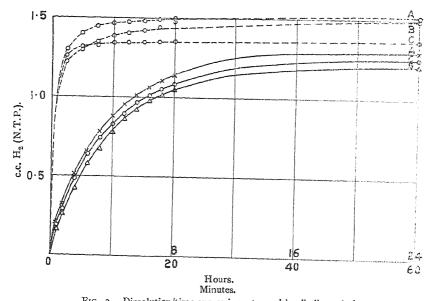


Fig. 3.—Dissolution/time curves in water and in alkaline solutions. A. Distilled water;  $p_{\rm H}=6.5$ . B. Saturated Mg(OH), solution;  $p_{\rm H} \approx 11^{\circ}$ 0.

C. o oor N KOH solution;  $p_{\rm H} = 12$  o. Broken curves are later stages.

decrease in the rate occurred in the presence of saponin, a result which, considered in conjunction with the facts already cited, represents a good case for anodic control.

#### Discussion of Results.

The primary hydroxyl ion discharge theory assumes that the initial anode reaction is not magnesium ion formation, but the discharge of hydroxyl ions which then combine with the metal.

The view of primary ion discharge was suggested by Sackur 4 and received support from Kistiakowsky, 5 Schoch 6 and Reichenstein. 7 The work of Le Blanc 8 on the decomposition potentials of alkali metal salts

<sup>&</sup>lt;sup>3</sup> Whitby, Trans. Faraday Soc., 29, 528, 1933 <sup>4</sup> Z. Elektrochem., 14, 612, 1908. <sup>6</sup> Trans. Faraday Soc., 9, 274, 1914. Z. physikal. Chem., 70, 200, 1910.

<sup>&</sup>lt;sup>7</sup> Z. physikal. Chem., 95, 457, 1920. 8 Ibid., 8, 299, 1891; 12, 333, 1893.

shows that the hydroxyl ion always undergoes preferential anodic discharge, except in fairly concentrated solutions of halides, when the halogen ion is discharged preferentially to the hydroxyl ion. These results were obtained with inert electrodes and in the case of anodes at which the discharged anion can react, it is certain that more negative potentials would be obtained, i.e., discharge would be facilitated. In the case of a reversible, or nearly reversible, anode reaction the difference between the reversible deposition potential of an anion and its observed potential at a reactive anode would be a measure of the free energy of the resulting compound, assuming that one compound only is formed. This is shown by the potential measurements of G. N. Lewis and coworkers of certain cells involving the discharge of chlorine or hydroxyl ions at mercury or silver electrodes.9 The deposition potentials of metallic kations at the dropping mercury electrode have been measured by Heyrovský, 10 who found that potentials obtained in this way were considerably less negative than their reversible electrolytic potentials, and who considered that the difference was a measure of the free energy of amalgam formation. For example, the reversible electrolytic potential of sodium is - 2.7v., but the deposition potential at the dropping mercury cathode is only -1.2v.

If an anode reaction can be considered reversible, therefore, and if the free energy of the resulting compound can be calculated or is known, together with the activities of the discharging anions at various dilutions and their free energies, then the discharge potentials of those anions can be calculated at the reactive anode. Assume that the discharge of hydroxyl, or O", ions at a magnesium anode, to form the sparingly soluble hydroxide or oxide, is reversible. The standard free energy of magnesium hydroxide may first be calculated. Beck  $^{11}$  gives — 1.856v. on the hydrogen scale as the electrode potential of magnesium in approximately  $^{1}M$  neutral magnesium sulphate solution. The activity coefficient of magnesium sulphate at this concentration is not known, but from Lewis and Randall's figures  $^{9}$  for more dilute solutions, it is probably about 0.07, which leads to -1.79v. for the standard electrode potential of magnesium.

$$\begin{split} & \text{Mg (S)} = \text{Mg}^{++}aq(a_{+}=1) + 2e. \quad \Delta F^{\circ}_{298} = -\ 82550 \text{ cals.} \\ \text{and} \quad \text{O}_{2}(\text{g. I atm.}) + \text{H}_{2}(\text{g. I atm.}) + 2e = 2\text{OH}'aq(a_{-}=1). \\ & \quad \quad \Delta F^{\circ}_{298} = -\ 74910 \text{ cals.}^{9} \\ \text{Mg}^{++}aq(a_{+}=1) + 2\text{OH}'aq(a_{-}=1) = \text{Mg}^{++}aq(a_{+}) \\ & \quad \quad \quad + 2\text{OH}'aq(a_{-}). \quad \Delta F = \text{RT } \ln\ (a_{+}\times a_{-}^{2}). \\ \text{Mg}^{++}aq(a_{+}) + 2\text{OH}'aq(a_{-}) = \text{Mg}(\text{OH})_{2}(S). \quad \Delta F = \text{O} \end{split}$$

where  $a_{+}$  and  $a_{-}$  are the individual ion activities in the saturated solution.

According to Kline, 12 the activity product constant of saturated magnesium hydroxide at 25° C., is 5 × 10<sup>-12</sup>,

.. 
$$RT \ln (a_+ \times a_-^2) = -15410 \text{ cals.}$$
  
 $\Delta F^{\circ}_{298} \text{Mg}(\text{OH})_2 = -172870 \text{ cals.}$ 

and

<sup>&</sup>lt;sup>9</sup> Lewis and Randall, *Thermodynamics*, McGraw Hill Book Co. <sup>10</sup> Phil. Mag., 45, 303, 1923. 
<sup>11</sup> Rec. Trav. Chim., 41, 353, 1922.

<sup>&</sup>lt;sup>10</sup> Phil. Mag., 45, 303, 1923.

<sup>12</sup> J.A.C.S., 51, 2093, 1929.

Now,

$$\begin{array}{l} \mathrm{Mg}(S) + \mathrm{O_2(g.\ I\ atm.)} + \mathrm{H_2(g.\ I\ atm.)} = \mathrm{Mg(OH)_2(S)}. \\ \Delta F^{\circ}_{298} = - \ \mathrm{I72870\ cals}. \\ \mathrm{2OH'} aq(a_- = \mathrm{I}) = \mathrm{O_2(g.\ I\ atm.)} + \mathrm{H_2(g.\ I\ atm.)} + 2e. \\ \Delta F^{\circ}_{298} = 74910\ \mathrm{cals}.^9 \\ \cdot \cdot \cdot \mathrm{Mg}(S) + \mathrm{2OH'} aq(a_- = \mathrm{I}) = \mathrm{Mg(OH)_2(S)} + 2e. \\ \Delta F^{\circ}_{298} = - 97960\ \mathrm{cals}. \end{array}$$

and if the hydroxyl ions are discharged from neutral solution, then  $\Delta F = \Delta F^{\circ}_{298} - 2RT \ln{(\rm I \times IO^{-7})} = -78860 \; {\rm cals.} = - \; {\rm I\cdot71}v.$  If the discharge of hydroxyl ions results in the formation of oxide and water, then,

$$\begin{array}{l} {\rm Mg}(S) + \frac{1}{2}{\rm O}_2({\rm g.~I~atm.}) = {\rm MgO}(S).~~ \Delta F^{\circ}_{298} = -~{\rm I}\,37000~{\rm cals.}^{13} \\ {\rm 2OH'}aq(a_- = {\rm I}) = \frac{1}{2}{\rm O}_2({\rm g.~I~atm.}) + {\rm H}_2{\rm O}(l) + 2e. \\ \qquad \qquad \qquad \Delta F^{\circ}_{298} = {\rm I}\,8350~{\rm cals.}^{9} \\ {\rm .\cdot.~Mg}(S) + {\rm 2OH'}aq(a_- = {\rm I}) = {\rm MgO}(S) + {\rm H}_2{\rm O}(l) + 2e. \\ \qquad \qquad \Delta F^{\circ}_{298} = -~{\rm I}\,18650~{\rm cals.} \end{array}$$

which, if the hydroxyl ion is discharged from neutral solution, gives  $\nabla F = -99550$  cals. = -2.16v., a value which is considerably more negative than the electrode potential of magnesium in neutral solution, showing that there is a greater tendency for the discharge of hydroxyl ions to form oxide than for the primary passage of magnesium ions into the liquid. Actually oxide may form first and then become hydrated, since magnesium-oxide calcined at low temperatures will easily hydrate. 14 The above calculations were performed on the assumption that the product forms a solid layer, but if a thin film of a saturated solution of the hydroxide is at first formed instead, the calculations would still remain the same. The potentials calculated are the decomposition potentials, and are those potentials at which discharge commences, and not necessarily those at which it continues. In the case of other anions, such as chlorine, bromine, iodine and sulphate, a soluble salt is formed, and the reaction will probably not be reversible, so that a similar calculation cannot be performed. Apart, however, from the results illustrated in the curves and already cited in support of preferential hydroxyl ion discharge, the theory is supported on other grounds. The free energies of magnesium chloride, bromide and iodide are lower than that of magnesium hydroxide and, although the reversible standard deposition potentials of chlorine, bromine and iodine at a platinum anode are more negative than that of the hydroxyl ion, the difference in the free energies of formation of the corresponding anodic compounds with magnesium is sufficient to indicate the tendency for primary preferential hydroxyl ion discharge. Unfortunately, free energy calculations can only indicate the tendency for a reaction to take place, and can give no idea of the velocity. Finally, there can be no doubt of the relative difficulty of discharge of the sulphate anion, which has a free energy of - 176500 cals.

The position is now clear for a consideration of the next stage in the mechanism of the dissolution of magnesium, and a short elaboration of the theory formulated in Part II. may be attempted. Many of the primary anodes of the magnesium surface (whether these are due to weak points in the air formed oxide film as postulated generally by

Parks and Kelly, J. Physical Chem., 30, 47, 1926.
 Anderson, J.C.S., 87, 257, 1905.

Evans, 15 or to lines of increased adsorption density, is immaterial) will, after the initial formation of a layer saturated with magnesium hydroxide, become covered with a film of hydroxide which will prevent further action by altering the potential of the surface, so that the film covered parts become cathodic to the remaining anodes. The rise in current density at the latter will result in an increased reaction rate at these points with consequent local impoverishment of hydroxyl ions and an increasing tendency, in the case of simple salt solutions, for the simultaneous discharge of the only other anion present. The rapid diminution in the number of primary anodes and the film formation at most of the initial points of attack can actually be observed. The usual view of the mechanism of film formation is somewhat vague, and it is generally considered that sparingly soluble hydroxide precipitated in the bulk of the solution, by double decomposition, is able to drift to the metal surface and to form there in some cases, a thin, uniform, adherent and protective film. Actually, the most efficient film formation would result from the direct discharge of hydroxyl ions at the metal surface, a mechanism which needs no ad hoc assumptions. The view of the direct formation of film is indeed sometimes recognised, since Evans has stated, 16 " the degree of adhesion of film depends partly on considerations of interfacial energy: but the substance is more likely to be adherent if it is the direct product of anodic attack."

The mechanism of the simultaneous discharge of two anions is elucidated somewhat by Fig. 4, which represents an ideal case, in which the current density/potential curves do not cross in the residual current range and in which the deposition potentials of the two ions are fairly close.

If A is the current density/potential curve for the hydroxyl ion and B the corresponding curve for the other anion of the solution, then hydroxyl ion alone will deposit until a current density is reached at which the other anion can deposit. If the current density is raised, the other anion will deposit in a proportion with A determined by the shape of the curves, but under any given conditions the fraction  $\frac{d_1}{d_1+d_2}$  of the total current will be utilised in depositing the hydroxyl ion and  $\frac{d_2}{d_1+d_2}$  in depositing the other anion. This, of course, assumes no impoverishment of anions at the anodes, and actually, as pointed out above, impoverishment of hydroxyl ion will probably occur, and will thus operate to deposit more of the more positive anion.

When only hydroxyl anions are present in the solution the reaction must inevitably come to a standstill, the actual amount of metal dissolved beforehand depending to some extent on the solubility of the hydroxide in the solution, or on the ability of the solution to peptise it. This fact is illustrated by Fig. 3 where it is shown that the reaction has practically ceased after 24 hours in water or in 0.001N potassium

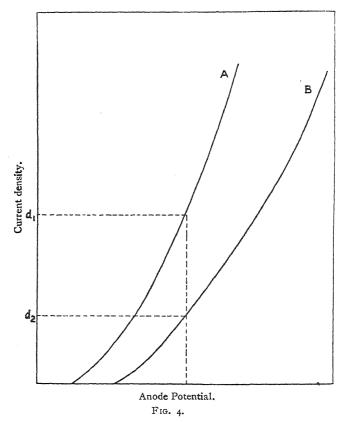
hydroxide solution.

In presence of other anions, if no sparingly soluble salt is formed, the number of permanent anodes will depend on a variety of factors, the most important of which will be the deposition potential of the anion in relation with that of the hydroxyl ion, the total volume and concentration

16 Trans. Faraday Soc., 19, 789, 1923.

<sup>16</sup> J.C.S., 92, 111, 1929; Trans. Amer. Electrochem. Soc., 57, 407, 1930.

of the solution, the area of the metal surface, the number and disposition of the primary anodes, the degree of agitation of the solution and the solubility of the hydroxide therein. When, for example, the chlorine anion finally discharges, a soluble salt is formed which diffuses away and forms magnesium hydroxide by double decomposition with the cathodic alkali, as postulated by the usual electrochemical view of corrosion. If traces of more noble metals of low overvoltage are dissolved at the same time, a redeposition will finally occur, and acceleration of the rate of reaction may take place. An example of this is illustrated by curve A, Fig. 1. If, however, the other anion forms a sparingly



soluble compound by simultaneous discharge with the hydroxyl ion, the reaction may come to a standstill as if the solution contained anions of hydroxyl only. Considerable amounts of iodine and bromine were detected in the film on magnesium corroded by potassium iodide and bromide, respectively, and this fact probably explains the rapid flattening of curves C and D in Fig. 1 compared with curve A for potassium chloride. Sulphate solutions form no basic salt with magnesium, but the deposition potential of the sulphate anion is so high that most of the primary anodes are covered with hydroxide before sulphate anions can discharge.

In very dilute solutions a high current density will be needed before other anions can discharge, and consequently the rates of attack will be similar in such solutions, irrespective of the nature of the dissolved salt. Fig. 2 illustrates the results from such solutions.

Effect of Solubility of Magnesium Hydroxide.—The solubility of magnesium hydroxide in the corroding solution will largely determine the life of the primary anodes as such, and therefore, the rate of attack will at first vary to some extent according to the solubility of the hydroxide. Fig. 3 shows that in spite of the higher hydroxyl ion concentration therein, 0.001N potassium hydroxide solution results in a lower final rate of attack than water. Fig. 1a shows that potassium sulphate solution initially produces a rate of attack greater than that given by either chloride, bromide or iodide, in spite of the high deposition potential of the sulphate anion, a fact which should result in a lower reaction rate. The explanation was thought to be due to a greater solubility of magnesium hydroxide in the IN potassium sulphate solution, and since no figures were available in the literature, some solubility determinations were carried out in water, 0.001N potassium hydroxide solution and normal solutions of potassium chloride, bromide, iodide and sulphate.

Gjaldbaek <sup>17</sup> found two modifications of magnesium hydroxide, the labile form of highest solubility being prepared by precipitation with bases or by the reaction between magnesium and water. Magnesium hydroxide prepared in the former manner was used in the present experiments and was washed free from soluble salts with hot water and dried at 95° C., until of constant weight. The solutions to be tested were made up from laboratory distilled water, redistilled from alkaline permanganate; A.R. reagents were used; 200 c.c. of each solution were placed in glass stoppered 250 c.c. measuring flasks. After allowing the temperature of the liquids to reach 25° C., by immersing the flasks in a water thermostat, 0·2 g. of magnesium hydroxide was introduced into each, and the flasks replaced in the thermostat for 3 weeks, and shaken every

At the end of the experiment the solutions were filtered through Gooch crucibles with pressure, and magnesium determined in the filtrates microgravimetrically by the hydroxyquinoline compound. The results expressed in gram-molecules per litre are recorded in Table II.; the figure obtained for water agrees well with the  $4.5 \times 10^{-4}$ 

TABLE II.—Solubilities of Magnesium Hydroxide in Various Solutions at 25° C.

Solutio	n.	Solubility.		
Water .		4.6 × 10 -4		
ooi N . KOH	[	2·2 × 10 -4		
N . KCl .		3·3 × 10 -4		
N . KBr .		2·9 × 10 -4		
N.KI.		3·2 × 10 -4		
$N \cdot K_{\mathfrak{s}} SO_{\mathfrak{s}}$		9.0 X 10 -4		

obtained by Gjaldback 17 at 18° C., by the conductimetric method.

The large increase in the solubility in normal potassium sulphate solution was expected, and confirms the view already expressed; the depression of the solubility caused by potassium hydroxide was also expected as already explained. The marked depression in the solubility caused by potassium chloride does not confirm the work of Palkin, 18 who has stated that the solubility of magnesium hydroxide is independent

<sup>17</sup> Z. anorg. Chem., 144, 145, 269, 1925.
18 Bull. Univ. Asie Centrale, 18, 73, 1929.

of the presence of potassium chloride. The solubilities in potassium chloride, bromide and iodide are almost the same, but cannot be applied to explain the rates of dissolution of magnesium in these solutions owing to the formation of sparingly soluble basic salts by simultaneous discharge of hydroxyl ions and bromine or iodine ions.

#### Relation between Surface Area and Rate of Attack.

The present writer is aware of no comprehensive experiments to obtain the relation between surface area of metal specimens and their rates of attack in corrosive solutions. It is generally assumed that a linear relationship exists, except, for example, when the rate of reaction is controlled by oxygen supply. In the case of magnesium in sodium chloride solution, the usual theory of primary chlorine anion discharge, if correct, would result in a rate of attack directly proportional to the surface area, unless edge attack were unduly prominent. Actually with magnesium the "edge effect" so often noticed with other metals is usually absent so that a direct relationship should exist.

The theory of primary hydroxyl ion discharge with simultaneous chlorine ion discharge only when the anodic current density is sufficiently high or when impoverishment of hydroxyl ions has occurred, prophesies, however, a rate of attack not in direct proportion to the surface area

of the specimens.

Consider a magnesium specimen immersed in a sodium chloride solution of fixed volume. Directly attack commences the hydroxyl ion concentration of the solution will rise, owing to discharge of hydrogen ions, and for the first few seconds the attack will probably be in direct proportion to the surface area of the specimens. The stirring due to hydrogen evolution will ensure a rapid admixture of these hydroxyl ions with the rest of the solution. Continuous attack of the metal can only take place when chlorine ion discharge commences, and this will occur after either a rise in the anodic current density or after local impoverishment of hydroxyl ions. This is tantamount to discharge of chlorine ions

only when the ratio [Cl]', has reached a critical figure, so that the greater the number of hydroxyl ions mixed with the fixed volume of chloride

solution the less likely is the critical ratio to be reached, and therefore, the number of permanent anodes in such cases will be smaller. Chlorine ion discharge takes place, after local anodic impoverishment of hydroxyl

ions, so that even if the critical  $\frac{[CI]'}{[OH]'}$  ratio is never reached in the bulk

of the solution, chlorine ion discharge can commence locally. In the case, therefore, of a small magnesium surface, the rate of attack should rapidly become disproportionately great in relation to larger surfaces.

In order to test the theory, magnesium sheet 0.18 mm. thick of composition corresponding to MgC<sub>2</sub> in Part I., was taken and, after cleaning in the usual manner, specimens I  $\times$  I·2, I  $\times$  4·2, 2  $\times$  4·I and  $2.5 \times 4.9$  cms. were cut and each punched with a hole 4.5 mms. diameter; in this way surface areas of 2, 8, 16 and 24 cms.2 were obtained. Each specimen was duplicated, and dissolution experiments were carried out in N, 0.1N and 0.01N solutions of both sodium chloride and sulphate. The specimens, after cleaning, remained in the corrosion vessel for about 18 hours before the solutions were added, which were always 50 c.c. volume. Hydrogen evolution measurements were made up to 75 hours

for each experiment, and the mean rates of attack were calculated after increasing times from commencement of the reaction, in cubic centimetres hydrogen evolved per hour. The calculations were made on the basis of the amount of hydrogen evolved between the time in question and the preceding reading, which for 10 and 20 minutes was 2 minutes before, for 2 hours 1 hour before, and for 27 and 75 hours, 3 hours before.

Some of the results are shown in Figs. 5 and 6, and after the preceding discussion need little comment. As expected, a direct proportion between rate of attack and surface area does not exist, smaller surfaces

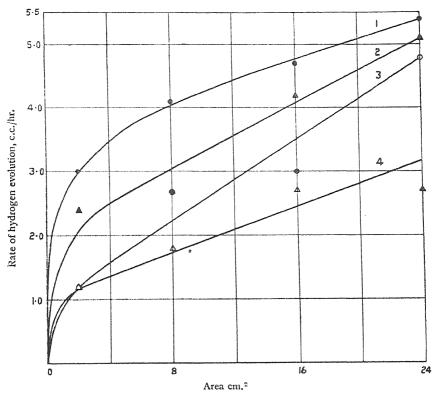


Fig. 5.—Effect of area on dissolution of magnesium in N/r sodium chloride and sodium sulphate solutions. Initial stages.

- 1. NaCl after 10 mins.
- 3. NaCl after 20 mins.
- 2. Na<sub>2</sub>SO<sub>4</sub> after 10 mins.
- 4. Na<sub>2</sub>SO<sub>4</sub> after 20 mins.

giving a rate of attack disproportionately large in relation to larger surfaces. This fact was checked by the number of points of complete penetration of the surface after 75 hours, which, per unit area, was greater the smaller the surface. The results for the O·IN and O·OIN solutions were similar, and are not shown for the sake of brevity.

#### Summary.

Experiments have shown that the initial rate of dissolution of magnesium in water, concentrated and dilute solutions of potassium chloride,

bromide, iodide and sulphate, and in solutions of alkali is always practically the same.

Experiments have been advanced in support of anodic control, and a theory of primary preferential hydroxyl ion discharge has been elaborated and supported by free energy calculations. Other anions can only discharge

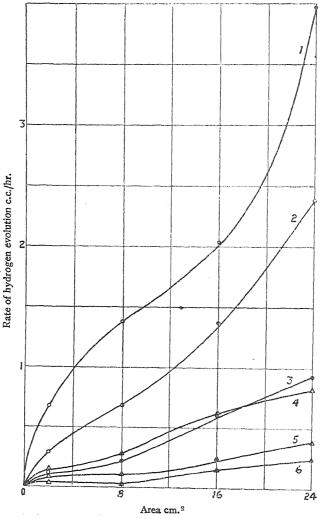


Fig. 6.—Effect of area on rate of dissolution of magnesium in N/1 sodium chloride and sodium sulphate solutions. Later stages.

- NaCl after 2 hrs.
- 2. NaCl after 27 hrs.
- 3. NaCl after 75 hrs. 4. Na<sub>2</sub>SO<sub>4</sub> after 2 hrs.
- 5. Na<sub>2</sub>SO<sub>4</sub> after 27 hrs.
  6. Na<sub>2</sub>SO<sub>4</sub> after 75 hrs.

when the anodic current density is high enough or when sufficient local impoverishment of hydroxyl ions has occurred.

The solubility of magnesium hydroxide has been measured in certain solutions, and its relation with rate of attack is discussed.

The relation between surface area and rate of attack of magnesium in

solutions of sodium chloride and sulphate has been investigated, and the rate has been found to be disproportionately great as the surface area is diminished. This result is shown to accord with the primary preferential hydroxyl ion discharge theory.

The work has been carried out for the Corrosion Research Committee of the Department of Scientific and Industrial Research; thanks are due to the Chairman, Professor Sir Harold Carpenter, F.R.S., and to Professor G. T. Morgan, F.R.S., Director of Chemical Research for permission to publish. The author is also indebted to Dr. G. D. Bengough for advice and interest.

Chemical Research Laboratory, Teddington, Middlesex.

#### REVIEWS OF BOOKS.

Grundlagen der Photochemie. By K. F. Bonhoeffer and P. Harteck. Pp. viii + 295 with 73 diagrams and 30 tables. Price 24 marks paper, 25 marks bound. (Theodor Steinkopff, Dresden and Leipzig, 1933.)

Recent years have witnessed the appearance of several excellent works on photochemistry. Although differing considerably in treatment and in scope, the books of Berthoud and of Kistiakowsky (1928), of Griffith and McKeown (1929), and of Style (1930) were, and are, all of real value. But this branch of chemical science continues to advance rapidly, and not only are theoretical views doubted, even discredited, which were held with some certainty a few years back, but also, in what is notoriously a difficult field of work, improved technique has led to a revision of supposed experimental facts in important instances. Whilst this is perhaps not a happy circumstance for authors, it makes the appearance of the present volume at this juncture particularly welcome to workers in and around the subject with which it deals.

The book is planned on sound lines. It opens with a brief chapter surveying existing photochemical data from the point of view of the law of photochemical equivalence. Chapter II. deals with primary processes. This is certainly the most important section, as it is the longest (171 pp.) of the book, and gives a very satisfying presentation of our knowledge (at the moment) of the process of the absorption of a light quantum by a molecule under the most diverse conditions, and of the immediate consequences which can follow its absorption. The treatment of such topics as electronic emission spectra and rotational quanta, whilst clear is brief, in accordance with the subject matter of the book, and the writer would single out for particular mention the luminous discussion of such subjects as transition probabilities, the average lives of activated states, the significance of the width of absorption lines and, in general, the whole complex of effects bound up with the differences between fine-structure bands, diffuse bands and continuous absorption, including absorption in

condensed systems. The chief classes of photochemically sensitive molecules are subsequently accorded separate treatment, and there is a series of valuable tables on pp. 26, 79, 80, 82.

Chapter III. is devoted to secondary processes, and opens with a useful synopsis of the fundamental formulæ of the gas kinetic theory and of general chemical kinetics. The chemical behaviour of excited atoms and molecules is then dealt with and our knowledge of the chemical reactivity of free atoms (particularly the H, O, and halogen atoms) summarised. In the last chapter, certain selected reactions are discussed in all their stages, ostensibly those "whose mechanisms can be regarded as definitely proved." The difficulty of such a choice is shown by the fact that the experiments of the Berlin school on the classical H<sub>2</sub>-Cl<sub>2</sub> reaction are taken as decisive. This judgment, to say the least, has been rendered very doubtful by the results contained in recent papers published from Cambridge, work which, incidentally, confirms in important respects earlier experiments made at Oxford.

This volume is the first of a number dealing with *Die Chemische Reaktion*, to appear under the editorship of Professors Mark and Polanyi, and forms an auspicious commencement of the series. The authors are well known as leading workers in the fields of thermal and photochemical kinetics and reactivity, and are eminently qualified for the task they have undertaken. Their book is an essential one for every photochemist, and it is to be hoped that it will also be read freely in wider circles.

Modern Thermodymics by the Methods of Willard Gibbs. By E. A. Guggenheim. With a Preface by F. G. Donnan (London: Metheun & Co. Ltd., 1933. Pp xvi. + 206. Price 10s. 6d. net.

It has always been recognised that the method of treatment of thermodynamics by Gibbs provided the most satisfactory basis of the science when anything beyond the elements of the subject was in question. The extreme aridity of Gibbs's work has repelled most students, although the mathematical equipment required is not very extensive. Mr. Guggenheim has had the happy idea of providing an exposition of Gibbs's methods, and at the same time linking up the chemical potential with modern developments as formulated in the conception of activity coefficients. The book practically assumes what Gibbs also took for granted, an acquaintance with the two laws, although it gives definitions of energy and entropy. In the range of subjects the usual choice is followed and the sections on solutions are probably the parts which will be found most useful. The section on Nernst's theorem is rather restricted, since the author believes that modern statistical mechanics is the only method which can be used for comprehensive treatment here. The book confines itself solely to general treatment, no quantitative or experimental illustrations making their appearance. For students who have made some progress in thermodynamics this book will be found interest. ing and one which will clarify and deepen their knowledge. For beginners it is probably rather too difficult. The book is very well printed and the price is very reasonable.

Catalysis and its Industrial Applications. By E. B. MAXTED, D.Sc., Ph.D., F.I.C. (London: J. & A. Churchill. Pp. xii and 530 with 66 figures and 225 tables. Price 36s. nett.)

This book accords admirably with its title. Part I. (pp. 1 to 406) is devoted to a general review of the general principles, theories and methods of catalysts, but the author has kept all the while in mind the present and future application of catalysis in industry. As an instance we may cite the chapter on hydrogenation where references are given to industrial hydrogenation processes such as that of naphthalene. Part II. is wholly concerned with industrial applications, such as the synthesis of ammonia, hydrogenation of oils and of coal, the oxidation of ammonia and the manufacture of sulphuric acid.

It is difficult in a short review to do justice to a work which covers a field which has now become so vast. All of it is interesting and valuable to readers of these transactions. It is not surprising that one turns first to see how the author treats subjects which have recently been the subject of General Discussion before this Society. In the forty-eight pages devoted to adsorption there is given an admirable summary of the subject, of which naturally the greater part is devoted to adsorption processes of special catalytic interest.

There is a very useful chapter of fifty-seven pages on the methods of preparation of the commoner catalytic materials. The chapter on laboratory methods has some useful hints on pressure vessels and joints.

In view of the great interest now being displayed in the catalytic hydrogenation of coal it is perhaps a little disappointing that the subject is dismissed in only four and a half pages.

The name index is an indication of the thoroughness and care with which the author has searched the literature in presenting his material. The subject index is, however, disappointingly incomplete.

The volume is excellently and carefully produced, but the price is too high.

Handbook of Mathematical Tables and Formulas. Compiled by Dr. R. S. Burington. (Handbook Publishers Inc. Sandusky, Ohio. Pp. 251.)

Part I. consists of formulæ and theorems from elementary mathematics. Part II. comprises a series of tables (4, 5, and 7 figure logarithms, natural and logarithmic trigonometric functions, etc.). The reviewer has found the book quite useful—although he has not found it necessary, except as a matter of interest, to consult one or two of the odd tables which are thrown in, such as "American Experience Mortality Table."

The book is clearly and well printed on strong paper, well-bound, and altogether well produced.

The Chemical Society. Annual Reports for 1932. (London: The Chemical Society, 1933. Pp. 344. Price 10s. 6d. Postage 6d.)

As usual this report is admirable and thorough. No chemist who wishes to keep abreast of the times can afford to be without it. In fact there must be many who, finding themselves wholly unable to read, much less to learn or inwardly digest, the vast mass of material which pours on their

library bookshelves weekly or monthly, will welcome this opportunity of knowing what has been happening in fields of knowledge outside their own special sphere. They only have to read the reports on matters of which they have intimate knowledge to realise the value of the other material which it is good they should know.

Reports of particular interest to readers of these *Transactions* are those of Mr. Wolfenden on Strong Electrolytes, on the Thermochemistry of Electrolytes and on Quantum Mechanics and Thermochemistry; of Mr. Hinshelwood on Chemical Kinetics; of Mr. Brown on Photochemistry and on the Structure of Simple Molecules; of Dr. Thompson on Flames and the Mechanism of Chemical Change; of Dr. Sidgwick on General Stereochemistry. The work of 1931-32 on sub-atomic phenomena and radioactivity has been reviewed by Dr. A. S. Russell.

As usual the report is carefully produced and admirably indexed.

Spectroscopy in Science and Industry: An Introductory Manual Describing its Applications to Industrial and other Practical Problems. By S. Judd Lewis, D.Sc. (London), D.Sc. (Tübingen), F.I.C., Ph.C., Lecturer in Spectroscopy at the Sir John Cass Technical Institute. (Blackie & Son, Ltd., London and Glasgow, 1933. Pp. viii + 94. Price 3s. 6d. net.)

Dr. S. Judd Lewis has written a compact book on Spectroscopy, which occupies rather less than 100 pages. Although it is essentially popular and practical in character, the scholarly quality of the work is shown in the early paragraphs by citations from original sources, of which the author appears to have made a first-hand study. The book was compiled with help from Mr. F. Twyman, and has the advantage of describing and figuring the best types of apparatus, as made by the firm of Adam Hilger. These include the new Spekker Spectrophotometer and the Echelon Cell first described by Mr. Twyman as recently as October, 1932.

Special attention is paid to quantitative methods which have been developed in connection with emission as well as absorption spectra, and a chapter is devoted to the "Ratio Quantitative System" described in *Chemistry and Industry* in 1932. Many illustrations are given of the uses of spectroscopy in industry and in analyses of the most diverse kind, ranging from the materials used in embalming in ancient Egypt, to samples of water recently sent from Cyprus.

The work has been well done, and the book will be of special value to those who are interested in the possible applications of spectroscopy in consulting and analytical practice.

L'Atome de Bohr. By Lêon Brillouin, Professeur à la Sorbonne. (Paris: Les Presses Universitaires de France, 1931. Pp. 363. Price 100 francs.)

The object of this book is to give a connected account of the older quantum theory and such parts of analytical dynamics, electrodynamics and relativity theory as have been found important in its development. Accordingly about one-third of the book is given up to a resume of the principal theorems of classical theory. As a knowledge of these is indispensable to any student of modern quantum mechanics, the book may well be regarded as a useful introduction to modern developments as well.

The account of the theory of quanta begins, as it should, with a statement of Bohr's correspondence principle, for this forms the natural step

from classical to quantum phenomena. Then follows an account of Sommerfeld quantum conditions and of the theory of electronic orbits in atoms. There is a clear and detailed account of atomic spectra, and the effect of electric and magnetic fields on them with an interesting chapter on the spinning electron.

The book is ably written, and can be strongly recommended to those who feel disposed to acquire familiarity with the old quantum theory before tackling the new.

Constitution of Atomic Nuclei and Radioactivity. By G. Gamow. (Oxford: at the Clarendon Press, 1931. Pp. 114. Price 10s. 6d.)

The author of this book was the originator of the theory of the spontaneous disintegration of nuclei, and is peculiarly fitted to write an account of the present position of experimental and theoretical knowledge of the nature of atomic nuclei. He has produced a most valuable and concise guide to this branch of physics with the minimum of mathematics.

The general features of the disintegration of nuclei by the emission of  $\alpha$  and  $\beta$  particles are described, and a summary is given of existing knowledge of the excited states of nuclei and their close connection with the emission of  $\gamma$ -rays. The difficulties of explaining the continuous nature of the  $\beta$ -ray emission from nuclei are stressed and the apparent conflict with the law of conservation of energy is pointed out. The book closes with a summary of the results so far obtained at Cambridge on the artificial transformation of nuclei by alpha particle bombardment.

Although the existence of the neutron was not known when this book was published, its discovery is not likely to upset the main conclusions stated by the author, though it may throw light on some of the unsolved problems which are discussed.

The Theory of Groups and Quantum Mechanics. By Hermann Weyl, translated from the second (revised) German edition by H. P. Robertson. (London: Methuen & Co., 1931. Pp. xvii + 422. Price 21s.)

Professor Weyl's book on "Gruppentheorie und Quantenmechanik" first appeared in 1928, and met with a warm reception from physicists and mathematicians. It aimed at stressing a parallelism between the concepts of the theory of groups, so highly developed by the mathematicians, and the concepts of quantum mechanics recently introduced by theoretical physicists. It therefore gave the essential features of group theory in a form suitable for the physicist and an account of quantum mechanics suitable for the mathematician. The book was very profound, and was difficult to read owing to the condensed style adopted by the author. The new German edition, of which this book is a translation, has expanded many of the arguments of the earlier edition and has aimed at a more elementary exposition.

Mathematics and physics alternate in the first four chapters of the book. The first gives an account of unitary geometry, the second of quantum theory, the third of the properties of groups, the fourth of the application of various groups to special problems in quantum mechanics. The last chapter contains among many profound applications a theory of the non-polar bond of chemistry.

This book will undoubtedly be purchased by every serious student of theoretical physics. Professor Weyl has a unique knowledge of both mathematics and physics, and whatever he writes bears the mark of distinction. All that need be said of the book is that it is certain to become a classic and is sure to exert a deep and abiding influence on physical thought.

J. E. L.-J.

Essai sur la Chimie Comparée. By Ionel N. Longinescu, D.Sc. Paris, Les Presses Universitaires de France, 1932. Pp. 98.

Professor Longinescu thinks that the comparative method, which has proved of such great value in the biological sciences, might be used with advantage in chemistry, in order to simplify the work both of the teacher and of the learner. He has, therefore, written a preliminary volume on "The Elements" fron this point of view, before extending his work to chemical compounds. In general his scheme is quite sound, but he has sacrificed nearly all its advantages by perpetuating Mendeleeff's classification (in which, for instance, hydrogen stands alone, instead of being grouped with helium as an initial family of two elements) and by ignoring almost completely the electronic structures of the various elements. Thus much greater clearness would have resulted if the author had merely introduced the Rydberg series as expressing the atomic numbers of the inert gases, and had made use of the contrast between elements which tend to lose electrons and those which tend to gain or share them, as providing the most obvious clue to the difference between metals and nonmetals. The book, in fact, is written from the standpoint of an earlier date than the nucleus atom, and can only be recommended as a convenient review of the properties of the elements as they appeared at this relatively undeveloped stage of modern atomic theory.

T. M. T.

The Cotton Effect and Related Phenomena. By Stotherd Mitchell, D.Sc. (London: G. Bell & Sons, Ltd.,1933. Pp. 92 with 34 diagrams. Price 7s. 6d.)

Dr. Stotherd Mitchell, whose papers on the "Asymmetric Photochemical Decomposition of Humulene Nitrosite by Circularly Polarised Light" and on the "Rotation, Dispersion and Circular Dichroism of Bornylene Nitrosite" have made him a recognised authority on this group of properties, has written a monograph on the "Cotton Effect and Related Phenomena," in which these interesting subjects are reviewed in a lucid and attractive manner. In particular, the monograph contains a historical review of the early work of Huygens, Malus and Fresnel, and of the phenomena discovered by Cotton in 1896 in aqueous solutions of coloured tartrates. Subsequent work on Rotatory Dispersion and Circular Dichroism in the region of absorption are reviewed in an important chapter, and a further chapter is devoted to the successful work of Werner Kuhn and of the author in preparing optically-active products by selective destruction of one form of a racemate by selective photochemical decomposition with circularly-polarised light. The experimental methods used in these lines of research are described and a bibliography of 125 entries is also given. The book is well written and well printed and can be recommended to all who are interested in the group of phenomena with which it deals.

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#### CORRIGENDA.

P. 683: The point A<sub>1</sub>O, Grams PbCl<sub>2</sub> 5.6 should be deleted.

P. 686: Reference 12 is: "Unpublished work from this laboratory."

In Table V all the figures in  $N_{\rm I}$ , except those three which are asterisked, should be divided by ten.

P. 949 (7 lines from bottom) should read:-

 $= F(\cos \phi_0, \pi/2) - F(\cos \phi_0, \psi_0),$ 

P. 950 (13th line) should read:-

can be put equal to  $(\epsilon' - \epsilon_2 + \Delta \cos^2 \alpha) \ z/\epsilon^2$ .

P. 986, line 4: transpose kg./cm.², to end of line which will then read—critical point, Fig. 3. The critical values for ethyl ether are 8 36.7 kg./cm.²,



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